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Revision 0

Preremedial Design Report of Remediation Options for OU 7-13/14

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September 2005

Idaho Cleanup Project

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Prepared for the
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ABSTRACT

This report presents the results of tests determining the effectiveness of treatment options for radioactive mixed waste and makes recommendations for their use in remediating the Subsurface Disposal Area, a radioactive landfill that is part of the Radioactive Waste Management Complex at the Idaho National Laboratory. The treatment options—in situ thermal desorption, in situ grouting, and ex situ grouting—were tested using transuranic waste from the landfill and surrogate.

The testing provides additional data that will aid the U.S. Department of Energy in determining the effectiveness of these options as treatments for waste at the landfill. These data will be used in preparing the remedial investigation and feasibility study for Waste Area Group 7, Operable Unit 7-13/14, to help evaluate the safety, effectiveness, and risk of these alternatives considered for the feasibility study. Remediation is being performed under the Comprehensive Environmental Response, Compensation, and Liability Act.

EXECUTIVE SUMMARY

This report presents the results of testing based on the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003) and makes recommendations for consideration during ongoing development of the feasibility study for Operable Unit (OU) 7-13/14. When the test plan was being prepared, the three treatment options (in situ thermal desorption [ISTD], in situ grouting [ISG], and ex situ grouting [ESG]) included in it were being evaluated and were all under consideration for use in developing remedial alternatives for the feasibility study. Since the test plan was written, data gathered through the test plan evaluations, the *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (Holdren and Broomfield 2004), and the *Feasibility Study Preliminary Documented Safety Analysis for In Situ Thermal Desorption in the Subsurface Disposal Area* (Abbott 2003) have led to the elimination of ISTD as a treatment option for the feasibility study. The results, conclusions, and recommendations from ISTD testing are included in this report to document testing conducted as a part of the test plan.

Grouts under consideration for ISG—neat[a] and with various admixtures—were tested for (1) durability, (2) characteristics that tend toward leaching or binding of contaminants, and (3) data to support contaminant transport modeling for treated waste forms. For ISTD testing, major emissions were quantified as waste and soil were slowly heated to determine the degree of hazardous organic contaminant and nitrate removal or destruction from the test samples. These tests were guided by the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003).

This report provides additional data for the U.S. Department of Energy to aid in determining the effectiveness of ISG and ESG as treatments for waste at the Subsurface Disposal Area (SDA). Some of the data generated during these tests will support the remedial investigation and feasibility study for Waste Area Group 7 OU 7-13/14.[b] The SDA is being remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (42 USC § 9601 et seq., 1980). The tests reported in this document address the Comprehensive Environmental Response, Compensation, and Liability Act criteria of effectiveness, both near and long term; reduction in mobility of contaminants through stabilization; and implementability. This document follows the organization and processes identified in guidance from the U.S. Environmental Protection Agency (EPA 1992).

In situ thermal desorption is commercially available and has been applied successfully at sites containing soil contaminated with organics (TerraTherm 2005a; Vinegar et al. 1998; Vinegar, Stegemeier, and Sheldon 1997); however, ISTD has not been demonstrated at sites containing buried containerized waste, radionuclides, nitrate salts, reactive mixtures, or large amounts of metal debris. The ISTD process under consideration uses electric resistance heaters to heat a region of the subsurface soil and waste to a prescribed temperature. Vapors generated by this heating process are collected and treated by an aboveground off-gas system. In situ thermal desorption can reduce the amount of contaminants in the subsurface by volatilization or, at higher temperatures, by degradation. Results from bench- and drum-scale tests and other evaluations (Abbott 2003) have shown that there are conditions where there is the potential to have uncontrolled reactions. In addition, there are conditions where ISTD may increase

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[a] Neat grout refers to any of the grout formulas that are used at 100% grout without waste or other additives. The neat grout was used as a baseline condition and compared with results when grouts were mixed with various waste loadings.

b. The *Federal Facility Agreement and Consent Order* (DOE-ID 1991) lists 10 WAGs for INL. Each WAG is subdivided into OUs. The RWMC is identified as WAG 7 and originally contained 14 OUs. Operable Unit 7-13 (TRU pits and trenches RI/FS) and OU 7-14 (WAG 7 comprehensive RI/FS) ultimately were combined into the OU 7-13/14 comprehensive RI/FS for WAG 7.

the mobility of some contaminants of concern. Because of these findings, ISTD is not recommended as a stand-alone treatment or a pretreatment for ISG at the SDA.

In situ grouting is being considered for treatment of transuranic (TRU) pits and trenches, and non-TRU pits and trenches and soil vault rows. Jet grouting is the specific ISG technique being considered for buried waste within the SDA. Jet grouting uses a specially designed rotary percussion drill rig to deliver and intimately mix grout with soil, debris, and contaminants in the subsurface. For purposes of this report, ISG will refer to jet grouting. The grout is injected at approximately 6,000 psi through small nozzles; high pressure combined with dense grout provides the energy required to mix the grout and subsurface materials. Each injection of grout in homogenous soil forms a column, and a series of diagonally offset columns forms a contiguous set of columns or monolith. Injection of grout in nonhomogenous waste can form columns with more variation in diameter, depending on voids and types of containers, but still interconnecting to form a monolith when a series of columns is placed in waste.

Grout must be designed specifically for ISG to meet the viscosity, particle size, and set times required for effective operation of the grouting rig. Past bench- and field-scale testing have demonstrated effectiveness and implementability of four of the grouts being tested. GMENT-12, U.S. Grout, TECT HG, and WAXFIX grout materials have been evaluated for leaching and physical characteristics to develop a recommendation of a single material for each application. Previous tests were conducted by Loomis et al. (2003) for application to TRU waste. The tests completed for this report were applicable to TRU, non-TRU, and Pad A waste. In addition to the proprietary grout formulations, five nonproprietary cementitious grout formulations (Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and thiosulfate, and Portland cement with slag and thiosulfate) were evaluated for immobilization of non-TRU radionuclides in soil. The primary component of each of these formulations, Portland cement, is the same as for GMENT-12, U.S. Grout, and TECT HG, making them viable alternatives for jet grouting; however, some additional tests would need to be conducted to verify that the nonproprietary grouts can be jet grouted and that they meet implementability criteria (Shaw 2004).

Ex situ grouting (solidification) is being considered for treatment of the Pad A salt waste. Ex situ grouting includes selection of an appropriate grout and an approach to transfer the waste from Pad A to a mixing system. This report examines only grout selection. Three candidate grouts[c] have been identified for testing as an ESG: Polysiloxane, Saltstone, and WAXFIX. Portland cement and other nonproprietary grouts generally do not handle high salt loads such as those that would be present in Pad A waste.

The tests in this report address six main objectives from Yancey et al. (2003):

- **Develop data to support contaminant transport modeling for treated waste forms.** Data obtained from these tests will be used in modeling migration of contaminants in the final waste form after ISG or ESG. In addition, these data will be used to determine changes in leachability of actinides from waste and surrounding soil following ISTD heating. These data will support modeling to estimate the release rate of contaminants from the treated waste and compare it to the predicted release rate from untreated waste. The test results also will support risk assessment, risk modeling, and performance evaluation portions of the feasibility study for OU 7-13/14.

c. Dimethyl Polysiloxane, marketed by Technology Visions Group, uses a polymer encapsulation technology (Loomis, Miller, and Prewett 1997) shown to successfully encapsulate surrogate salt materials. Saltstone grout, developed by Savannah River Site, has been developed for salt encapsulation. WAXFIX also is considered in the in situ portion of Yancey et al. (2003).

- **Evaluate durability of grouted waste.** Physical property data will be obtained to compare grouts and waste loadings. Long-term physical stability of the grouted waste forms will be estimated from these near-term tests.

- **Evaluate WAXFIX for use as a grout.** The purpose of these tests is to understand better the advantages and limitations of WAXFIX as a grout for TRU and non-TRU waste. Data will be used to address potential criticality and reactivity concerns that may be encountered with specific types and concentrations of contaminants. The ability of WAXFIX to contain radionuclides and nitrates is evaluated. In addition, the generation rate of hydrogen gas for WAXFIX mixed with radionuclides will be assessed because of the radiolysis process.

- **Quantify major emissions as waste and soil are slowly heated.** Determining primary off-gas constituents and concentrations as waste and soil are heated will help identify the off-gas processing requirements for full-scale test planning. The carbon monoxide and carbon dioxide releases determine the relative amounts of combustion and pyrolysis occurring. The gas proportion measurements also could assist in monitoring the type of waste being heated and any nitrate organic reactions. In addition, these data will support the generation of safety and design data for OU 7-13/14.

- **Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste.** Quantifying the removal or destruction of chlorinated volatile organic compounds (VOCs) and nitrate salts in the waste will help establish anticipated efficiency of ISTD-mediated removal or destruction of contaminants of concern in TRU pits and trenches waste. Data also will be used to generate design data for the pending feasibility study for OU 7-13/14.

- **Test potential mixtures of organics and nitrates for reactivity.** Determining whether mixtures of nitrate salt sludge and organic sludge will react exothermically during heating by ISTD will help establish temperature ranges to avoid such reactions.

The ISTD testing raised, as well as answered, questions about applicability of ISTD to the SDA. Nitrate salts are expected to react exothermically with various forms of carbon in the waste. As shown most clearly in the thermal gravimetric analysis tests, the chemical form of carbon and rate of temperature increase of the system affect the magnitude and intensity of the reaction. The drum-scale reactivity experiments failed to demonstrate a method to heat nitrate salt surrogate and carbon-containing materials in a manner that maintained control over reaction between nitrate and carbon. Based on thermal gravimetric analysis and drum-scale results, it may be possible to heat mixtures of nitrate and carbon-containing waste in a manner that keeps the reaction under control, but it would require slow rates of heating and control of hot-spot formation. In a heterogeneous, uncharacterized waste form (i.e., containing organics and nitrates), such as exists in the SDA, the potential for uncontrolled exothermic reactions exist. Therefore, ISTD could not be implemented safely based on the results of the bench- and drum-scale tests.

In situ thermal desorption should be able to remove VOCs and oils from the subsurface through a combination of volatilization, oxidation, and reduction. The fate of radionuclides during ISTD cannot be conclusively stated based on data collected during this testing. Elimination of organic compounds and nitrate would simplify and improve the overall performance of grout in the waste; however, all of the grouts tested can tolerate the presence of some amount of organic and nitrate compounds. Elimination of only the VOCs would significantly reduce the inventory of chlorinated organic compounds, some of which are contaminants of concern, and would reduce by about half the total mass of organic compounds present in the waste. The removal of VOCs could likely be done at temperatures below 230°C (446°F) to avoid the nitrate-cellulose reaction, but additional testing and modeling would be required to demonstrate

the technical and economic feasibility of this approach. By reducing the total mass, grouting will work more effectively by increasing the amount of grout that can be injected into the waste, thus decreasing the waste-to-grout ratio; however, because of the potential for uncontrolled exothermic reactions and the potential to increase contaminant mobility in some cases, ISTD is not recommended at the SDA.

The ISG tests did not demonstrate one grout formulation to be significantly better than the other grout formulations for all radionuclides and waste forms evaluated. The waste loadings used in the leach tests were determined by the maximum amount of waste or surrogate that could be added to the grout and still maintain a cohesive sample. Although the leach index was expected to decrease as waste loading increased, this was not observed. For many of the samples containing TRU isotopes (i.e., uranium, americium, plutonium, and neptunium), the concentrations of radionuclides in the leachate were below the detection limit; therefore, the leach index was calculated from the detection limit. For the samples containing TRU isotopes, most of the leach indices (with the exception of neptunium) are greater than 10, indicating low effective diffusivity and high resistance to leaching. Because most data came back nondetectable, the leach indices did not vary much either.

Radionuclides were added at concentrations that were detectable in the untreated waste; therefore, all of the grouts were successful at reducing the leachability of the radionuclides tested. If the grout functions only as a macroencapsulation agent, then chemistry of the radionuclide is not important. If the grout immobilizes contaminants through a combination of chemical interaction and macroencapsulation, such as is the case with cementitious formulations, then chemistry of the contaminant is important. For this reason, the TRU radionuclides may behave differently from non-TRU radionuclides, with respect to leaching, when grouted in cementitious materials. The leach index values for all the radionuclides (TRU and non-TRU) were approximately the same in WAXFIX. This is not surprising since WAXFIX works by encapsulation of the contaminant. For all of the samples containing non-TRU isotopes (i.e., carbon, technetium, and iodine), concentrations of the radionuclides in the leachate were above detection limits. The leach index of non-TRU isotopes was generally lower than that for TRU isotopes in U.S. Grout and TECT HG. Cementitious grouts immobilize contaminants through a combination of chemical interaction and encapsulation. The difference seen between the two classes of radionuclides within the cementitious grouts is probably caused by a difference in the chemical interactions between the radionuclides and the grouts.

The radionuclide, as well as the type of waste matrix, is important to evaluating a grout for use as a stabilization material. Compressive strength, porosity, and hydraulic conductivity are important parameters to consider when evaluating the immobilization potential of a grout for a specific contaminant, but none of them are a direct indicator of leach resistance. The addition of waste materials generally decreased the compressive strength and increased the hydraulic conductivity and porosity of the grouts compared to neat grout samples. These measurements suggest that the ability of grouts to immobilize contaminants decreased with the presence of waste. Based on results of ANS leach tests conducted on grouted samples alone, there is no clear best choice among formulations of grouts tested for all types of waste and contaminants. Based on current testing and past studies, the strongest performing grouts, considering physical properties, leaching, and cost, for each class of contaminant and waste are as follows:

- For TRU contaminants in soil, four grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In areas where physical support and immobilization of contaminants is needed, GMENT-12 would be preferred, as it performed the best overall.

- For TRU contaminants in organic sludge, four grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In this case, all of the grouts performed equally well at reducing leachability of TRU contaminants, but GMENT-12 had the highest compressive strength. If organic sludge is to be grouted and if compressive strength is important, then GMENT-12 would be the best choice.

- For TRU contaminants in nitrate salt, five grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, and Saltstone. In areas where carbon steel drums or nonmetal containers were used to contain TRU contaminants in nitrate salt, the integrity of the containers is likely already compromised, and jet grouting could be used to reduce the potential for contaminant transport. Where ISG has been identified for use in nitrate salts, U.S. Grout is recommended because it produces samples with the highest compressive strength and a comparable leach index to the other grouts tested. WAXFIX also produced good leach-resistant samples and could withstand high salt loadings; however, the compressive strength was not as good as U.S. Grout.

- For non-TRU contaminants in soil, ten grout formulations were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, Saltstone, Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and thiosulfate, and Portland cement with slag and thiosulfate. Portland cement with slag, Portland cement with slag and thiosulfate, WAXFIX, and GMENT-12 would be the best and essentially equal choices for immobilization of C-14, Tc-99, and I-129 in soil. Based on physical properties, GMENT-12 compared to Portland cement with slag has the same compressive strength and porosity and lower hydraulic conductivity. WAXFIX compared to GMENT-12 and Portland cement with slag has lower compressive strength, lower porosity, and equal hydraulic conductivity. If cost is considered, then Portland cement with slag will be the best choice.

- WAXFIX is recommended for ESG of nitrate salt waste. Most Portland cement-based grouts do not tolerate high loadings of salts. Based on the test results, Saltstone, a Portland cement-based grout, might work effectively with some modification to the recipe used in this report. WAXFIX, a paraffin based grout, was able to tolerate high concentrations of salts and maintain a cohesive sample.

- If ISG were used for physical support of a cap, then a cementitious grout would be the preferred choice. Overall, Portland cement with slag, GMENT-12, or U.S. Grout would be the best choices for physical support of the cap. Based on unconfined compressive-strength tests, GMENT-12 was the most tolerant of organic sludge, U.S. Grout was the most tolerant of nitrate salt, and soil was tolerated equally by all three. Since nonproprietary grouts, such as Portland cement with slag, are expected to be less expensive than proprietary grouts, and since volume percentage of organic sludge and nitrate salt waste in the SDA is relatively small, Portland cement with slag is recommended for use as a cap support grout in the SDA.

ACKNOWLEDGEMENTS

This report embodies the cooperative effort of numerous technical and support staff, without whose many contributions and commitment to excellence this work would not have been possible. The authors would like to recognize and express their gratitude to John Dick, Rick Demmer, Bruce Mincher, Robert Kirkham, Kristine Baker, Alan Herbst, Steve Johnson, and Marvin Banks who performed experimental work, drafted appendixes, and contributed to sections of this report.

CONTENTS

FIGURES

TABLES

ACRONYMS

ANS	American Nuclear Society
COC	contaminant of concern
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
ESG	ex situ grouting
ICP-MS	inductively coupled plasma-mass spectrometry
INL	Idaho National Laboratory
ISG	in situ grouting
ISTD	in situ thermal desorption
K_d	partition coefficient
OU	operable unit
PNNL	Pacific Northwest National Laboratory
RFP	Rocky Flats Plant
RI/FS	remedial investigation and feasibility study
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
TGA	thermal gravimetric analysis
TRU	transuranic
VOC	volatile organic compound
WAG	waste area group

Preremedial Design Report of Remediation Options for OU 7-13/14

1. INTRODUCTION

This report presents results of testing based on the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003) and makes recommendations for consideration during development of the feasibility study for Operable Unit 7-13/14. Grouting treatment options are being considered for radioactive waste buried in the Subsurface Disposal Area (SDA), a radioactive landfill that is part of the Radioactive Waste Management Complex (RWMC) at the Idaho National Laboratory (INL) Site (see Figure 1). The grouting treatment options include in situ grouting (ISG) and ex situ grouting (ESG). In addition to grouting, in situ thermal desorption (ISTD) was evaluated.

When the test plan (Yancey et al. 2003) was prepared, the three treatment options (ISTD, ISG, and ESG) included in it were being evaluated and were all under consideration for use in developing remedial alternatives for the feasibility study. Since the test plan was written, data gathered through the test plan evaluations, the *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (Holdren and Broomfield 2004), and the *Feasibility Study Preliminary Documented Safety Analysis for In Situ Thermal Desorption in the Subsurface Disposal Area* (Abbott 2003) have led to the elimination of ISTD as a treatment option for the feasibility study. The results, conclusions, and recommendations from ISTD testing are included in this report to document the testing conducted as a part of the test plan by Yancey et al. (2003).

In situ grouting and ESG can physically stabilize waste and slow the release and migration of most hazardous inorganics and radionuclides. In addition, ISG-treated areas of the SDA can minimize subsidence and support a future surface barrier to reduce water infiltration into the waste. In situ thermal desorption focuses on removal of organics but also can remediate nitrate salts and chlorinated organics in organic sludge.

Grouts under consideration for ISG—neat and with various admixtures—were tested for (1) durability, (2) characteristics that tend toward leaching or binding of contaminants, and (3) data to support contaminant transport modeling for treated waste forms. For ISTD testing, major emissions, quantified as waste and soil, were slowly heated to determine the degree of hazardous organic contaminant and nitrate removal, or destruction from test samples. Potential mixtures of organics and nitrates were tested for reactivity. These tests were guided by the test plan by Yancey et al. (2003).

1.1 Purpose

This report provides additional data for the U.S. Department of Energy to aid in determining the effectiveness of ISG and ESG as treatments for waste at the SDA. Some of the data generated during these tests will support the remedial investigation and feasibility study (RI/FS) for Waste Area Group (WAG) 7 Operable Unit (OU) 13/14.[a] The SDA is being remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (42 USC § 9601 et seq., 1980). The tests reported in this document address Comprehensive Environmental Response, Compensation, and Liability

a. The *Federal Facility Agreement and Consent Order* (DOE-ID 1991) lists 10 WAGs for INL. Each WAG is subdivided into OUs. The RWMC is identified as WAG 7 and originally contained 14 OUs. Operable Unit 7-13 (TRU pits and trenches RI/FS) and OU 7-14 (WAG 7 comprehensive RI/FS) ultimately were combined into the OU 7-13/14 comprehensive RI/FS for WAG 7.

Act criteria of effectiveness, both near and long term; reduction in mobility of contaminants through stabilization; and implementability. This document follows the organization and processes identified in guidance from the U.S. Environmental Protection Agency (EPA 1992).

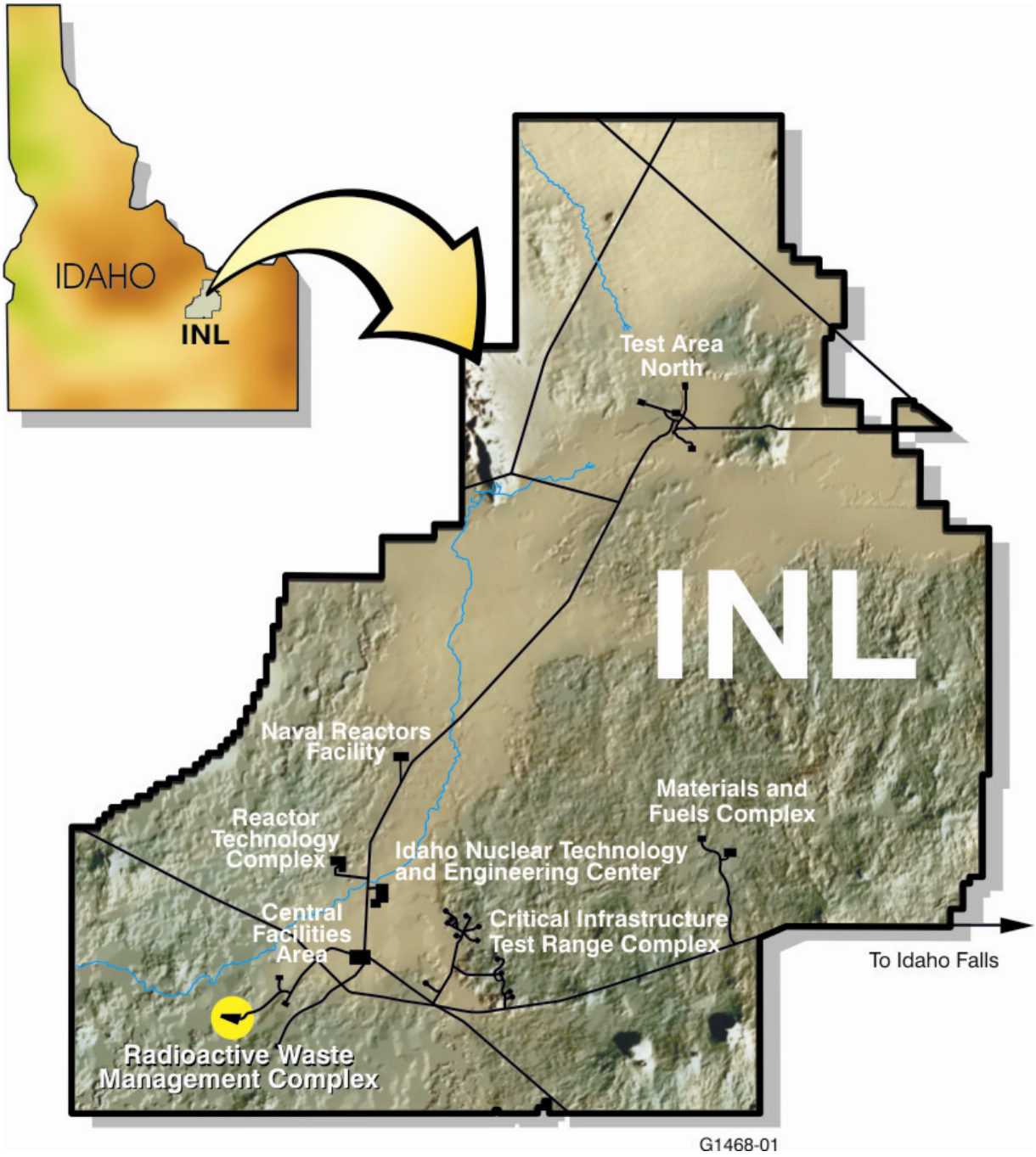

Figure 1. Map showing Radioactive Waste Management Complex and other major facilities.

1.2 Scope

The tests reported in this document focus on thermal treatment and stabilization of radioactive mixed waste buried in the SDA and follow Yancey et al. (2003). Twenty tests are described, and the results are reported in this document.[a] Based on results of the originally planned tests, four tests (hydraulic conductivity, porosity, compressive strength, and leaching) were repeated with four additional grout formulations. Tests for ISTD and ISG used transuranic (TRU) waste from the SDA and surrogate. The ISG tests also used surrogate non-TRU waste. The ESG bench tests used waste from Pad A.

A series of cold (nonradioactive) tests established the approach for hot (radioactive) testing. Hot tests used surrogates spiked with radionuclides (isotopes of uranium, plutonium, americium, neptunium, iodine, carbon, and technetium were used, as appropriate, for specific tests), waste material retrieved from Pit 9 by the OU 7-10 Glovebox Excavator Method Project (DOE-ID 2004), and material from Pad A. All preparations for hot testing, including safety documentation, were completed before accepting material from Pit 9 or Pad A and are documented separately.

The screening process in Zitnik et al. (2002) streamlined the list of available remedial technologies and process options, retaining for subsequent development and screening only those that met the criteria adequately. The effectiveness of these remaining technologies is presented in this report through results of bench and laboratory tests.

1.3 Site Description

The Idaho National Laboratory Site is located in southeastern Idaho and occupies 2,305 km^2 (890 mi^2) in the northeastern region of the Snake River Plain. Regionally, the INL Site is nearest to the cities of Idaho Falls and Pocatello and to U.S. Interstate Highways I-15 and I-86. The INL Site extends nearly 63 km (39 mi) from north to south, is about 58 km (36 mi) wide in its broadest southern portion, and occupies parts of five southeast Idaho counties. Public highways (i.e., U.S. 20 and 26 and Idaho 22, 28, and 33) within the INL Site boundary and the Experimental Breeder Reactor I, which is a national historic landmark, are accessible without restriction. Otherwise, access to INL Site is controlled. Neighboring lands are used primarily for farming or grazing, or are in the public domain (e.g., national forests and state-owned land) (Zitnik et al. 2002).

The SDA landfill, established in 1952, was originally called the National Reactor Testing Station Burial Ground. The original landfill covered 5.2 ha (13 acres) and was used for shallow land disposal of solid radioactive waste. In 1958, the SDA was expanded to 36 ha (88 acres). Relocating the security fence in 1988 outside the dike surrounding the SDA established its current size of 39 ha (97 acres). The Transuranic Storage Area was added to the RWMC in 1970. Located next to the east side of the SDA, the Transuranic Storage Area's 23 ha (58 acres) is used to store, prepare, and ship retrievable TRU waste to the Waste Isolation Pilot Plant, southeast of Carlsbad, New Mexico. The 9-ha (22-acre) administration and operations area at the RWMC includes administrative offices, maintenance buildings, equipment storage, and miscellaneous support facilities (Holdren et al. 2002). See Figure 2 for a map of the physical layout of all RWMC disposal locations and facilities.

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b. After the test plan was completed, four tests—macroencapsulation, microencapsulation, plutonium aerosolization, and fracture propagation—were delayed until results of tests recorded in this report were available. These four tests originally were described in the test plan but had not been conducted at the time this report was written.

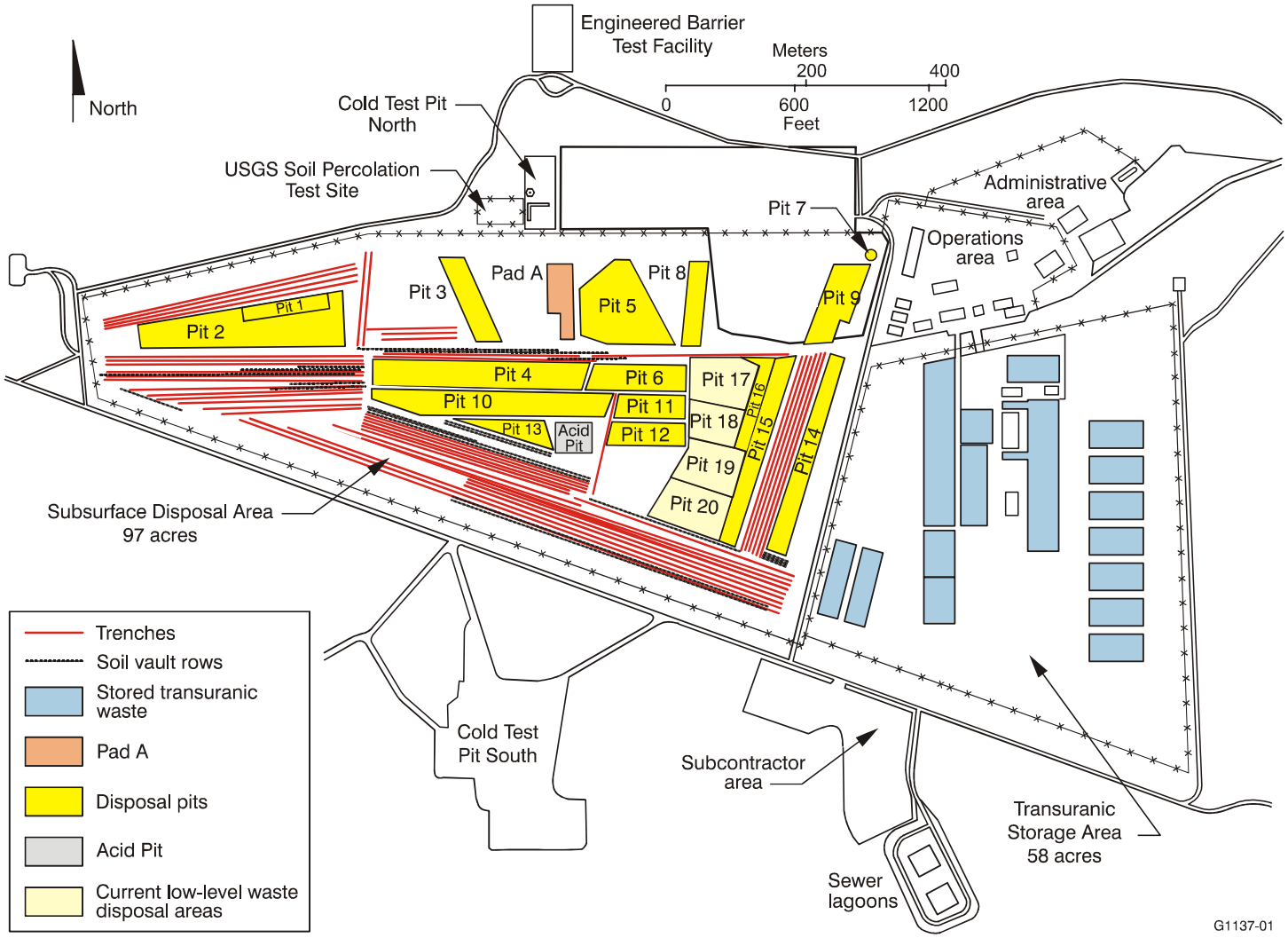

Figure 2. Map of the Radioactive Waste Management Complex showing the location of the Subsurface Disposal Area and types of buried waste.

1.3.1 Brief History of Site Operations

Disposal of mixed waste containing hazardous chemical and radioactive contaminants was allowed through 1984. Since 1985, waste disposals in the SDA have been limited to low-level radioactive waste generated at the INL Site. Construction, operation, and decommissioning of INL programs for nuclear reactor testing have resulted in large volumes of waste. Various containers were used in shipping and disposing of waste, including steel drums, cardboard cartons, and wooden boxes. Larger, individual items—such as tanks, furniture, process and laboratory equipment, engines, and vehicles—were placed separately as loose trash (Zitnik et al. 2002).

Contaminants—disposed of in shallow subsurface disposal units consisting of pits, trenches, and soil vaults—include hazardous chemicals, remote-handled fission and activation products, and TRU radionuclides. Disposals of TRU and mixed waste—mostly from Rocky Flats Plant (RFP) in Colorado—were allowed through 1970. Radioactive waste from offsite sources originated from a variety of facilities, including military and other defense agencies, universities, commercial operations, and the Atomic Energy Commission (Zitnik et al. 2002).

1.4 Description of Buried Waste

Several waste types at the SDA include the nitrate salts in Pad A and combustibles, soil, and three types of sludge (inorganic, organic, and nitrate salt) in TRU and non-TRU pits and trenches. Based on recent mapping and burial records, nitrate or organic sludge drums are found in 20% or less of four pits (Becker et al. 1998; Salomon et al. 2003). The density of organic sludge drums is usually less than 4.5 drums/m^2; the density of nitrate salt drums is less than 1.6 drums/m^2. High-density areas greater than this occur in less than 10% of the total drum area. Thus, areas of high density are rare.

The results presented in this report are from tests conducted with surrogates and wastes. The surrogates were prepared based on the expected composition of the waste and with and without radionuclides (hot and cold surrogates, respectively). The wastes were[d] samples retrieved from locations within the SDA, that is organic sludge waste was retrieved from Pit 9 and Pad A waste was retrieved from Pad A. The primary TRU contaminants of concern (COCs) that were used in this study are americium, plutonium, uranium, and neptunium. The non-TRU COCs include technetium, iodine, and C-14 (Holdren et al. 2002).

1.4.1 Organic Sludge Waste and Surrogate

Organic sludge from Pit 9 contains chlorinated volatile organic COCs, such as trichloroethene, trichloroethane, tetrachloroethene, methylene chloride, and carbon tetrachloride, in addition to the TRU COCs (Holdren et al. 2002). Two different estimates of organic sludge waste compositions have been developed based on several reports: Clements (1982), Vigil (1990), Liekhaus (1991), and Arrenholz and Knight (1991). The earlier 1982 and 1989 assessments gave the approximate organic liquid content of SDA sludge based on sludge preparation and shipping records. The 1991 assessments have been updated based on the following:

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[d] Samples were taken during operation of the OU 7-10 Glovebox Excavator Method Project, which retrieved 59 m^3 (77 yd^3) of buried waste from the SDA during December 2003 and January 2004 (DOE-ID 2004). The purpose of the Glovebox Excavator Method Project was to demonstrate the feasibility of waste retrieval, provide information on any COCs present in the underburden, and characterize waste-zone material for safe and compliant storage pending a decision on final disposition. The Glovebox Excavator Method Project operated under the *Federal Facility Agreement and Consent Order for the Idaho National Engineering Laboratory* (DOE-ID 1991) and the "Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA/Superfund)" (42 USC § 9601 et seq., 1980).

- Calculations from recent vapor removal by the Organic Contamination in the Vadose Zone system
- Newly found records as RFP sludge preparation areas are decontaminated
- Recent shallow sampling of organic vapor between waste pits.

The current composition is now hypothesized to be 21 to 27 vol% Texaco Regal Oil,[e] 11 to 23 vol% miscellaneous oil, 20 to 37 vol% carbon tetrachloride, and 30 vol% other chlorinated hydrocarbons (details of the composition are presented in Appendix A).

The primary halogenated hydrocarbon COC in the organic sludge is carbon tetrachloride. Calcium silicate, Oil Dri, Microcel E, or other sorbent material was added as an absorbent for organic liquids (Texaco Regal Oil) (Miller and Varvel 2005). The Texaco Regal Oil used at RFP is no longer manufactured.

1.4.2 Pad A Waste and Nitrate Salt Sludge

Composition of Pad A waste includes salt at 30 wt% potassium nitrate and 60 wt% sodium nitrate flakes with about 400 ppm soluble chromate (such as Cr^{+6}) and 180 pCi/g uranium as the primary hazardous and radioactive components (a detailed composition is provided in Appendix A). While nitrate and total chromium are issues with the nitrate salt sludge, the only contaminant of concern is uranium. The primary components of nitrate salt sludge (RFP Series 745 sludge) are sodium nitrate and potassium nitrate in an approximate 2-1 ratio. The composition of the Pad A waste and the nitrate salt sludge waste are essentially the same. Since nitrate salt sludge waste was not retrieved from Pit 9, Pad A waste was used for testing. Nitrate salt sludge surrogate (without radionuclides) was also prepared for testing as required. The nitrate salt sludge COCs are nitrates and uranium (Holdren et al. 2002).

1.4.3 Inorganic Sludge Surrogate

The inorganic sludge surrogate formulation is based on average composition of inorganic precipitates in original RFP Series 741 and 742 sludge (Landman 1981; Clements 1982) and previous surrogates developed to represent this sludge (Low 1985; Low et al. 1987; Loomis and Low 1988) as shown in Appendix A. The inorganic sludge surrogate will contain RWMC lake-bed soil, other inorganic salt, water with terbium added, and nitrate salt. The RFP waste is estimated to have contained 40 to 70 wt% water, to which 10 to 20 wt% cement was added when the sludge was placed in drums. At 20 wt% cement, the sludge-cement mixture would likely resemble a consolidated rather than an unconsolidated material. To be conservative with respect to evaluating the performance of ISG and ISTD, the amount of water and cement has been minimized to maximize the concentration of inorganic salts and create an unconsolidated material. This approach is consistent with previous testing activities (Low 1985; Low et al. 1987; Loomis and Low 1988).

1.5 Document Organization

The following paragraphs briefly describe the remaining sections in this report:

- Section 2 describes treatment technologies under consideration
- Section 3 introduces testing

e. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise do not necessarily constitute or imply endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho Cleanup Project at the Idaho National Laboratory Site.

- Section 4 discusses each test series for ISTD and integrates the results
- Section 5 discusses each test series for ISG and integrates the results
- Section 6 discusses each test series for ESG and integrates the results
- Section 7 contains conclusions and recommendations
- Section 8 lists the references cited throughout this report
- Appendix A contains the recipes used in the tests and details of compositions mentioned in the body of the report
- Appendixes B through T describe the study approach and test design and contain the results for each test series.

2. DESCRIPTION OF TREATMENT TECHNOLOGIES

The following sections describe the three treatment technologies—ISTD, ISG, and ESG—for which evaluation data were collected during this study.

2.1 In Situ Thermal Desorption

In situ thermal desorption is commercially available and has been applied successfully at sites containing soil contaminated with organics (TerraTherm 2005a; Vinegar et al. 1998; Vinegar, Stegemeier, and Sheldon 1997); however, ISTD has not been demonstrated at sites containing buried containerized waste, radionuclides, nitrate salts, reactive mixtures, or large amounts of metal debris. In situ thermal desorption was being considered for areas in the SDA with high concentrations of volatile organic compounds (VOCs). The ISTD process considered using electric resistance heaters to heat a region of the subsurface soil and waste (see Figure 3) to a prescribed temperature. Vapors generated by this heating process are collected and treated by an aboveground off-gas system. In situ thermal desorption can reduce the amount of contaminants in the subsurface by volatilization or, at higher temperatures, by degradation. Results from bench- and drum-scale tests presented later in this report have shown that there are conditions where potential to have uncontrolled reactions exists. Other evaluations (Abbott 2003) have identified the potential consequences of uncontrolled reactions. Because of these findings, ISTD is not recommended as a stand-alone treatment or a pretreatment for ISG at the SDA. The discussion that follows describes the ISTD system and presents the results of the evaluations performed.

In most applications of ISTD, two types of boreholes are used. One type provides heat and vapor removal; it contains an electrical resistance heater within a sealed metal pipe. The metal pipe sits within a perforated metal casing. Vapor is removed through the annulus between the two pipes. The second type of borehole provides heat only; it also contains an electrical resistance heater in a sealed pipe, which is also closed at the surface. The boreholes are spaced 2.1 to 3 m (7 to 10 ft) apart (U.S. Navy 1998) for removal of higher boiling-point compounds and 3 to 6.1 m (10 to 20 ft) apart for lower boiling-point compounds (TerraTherm 2005a). Heat is transferred to surrounding media by conduction. Heating boreholes are placed around heating-and-vapor-removal boreholes (see Figure 3). Heaters in boreholes can operate at temperatures of up to 1,000°C (1,832°F) (U.S. Navy 1998; Abbott 2003), although generally they operate at 400 to 800°C (752 to 1,472°F) (TerraTherm 2005a; Yancey et al. 2003).

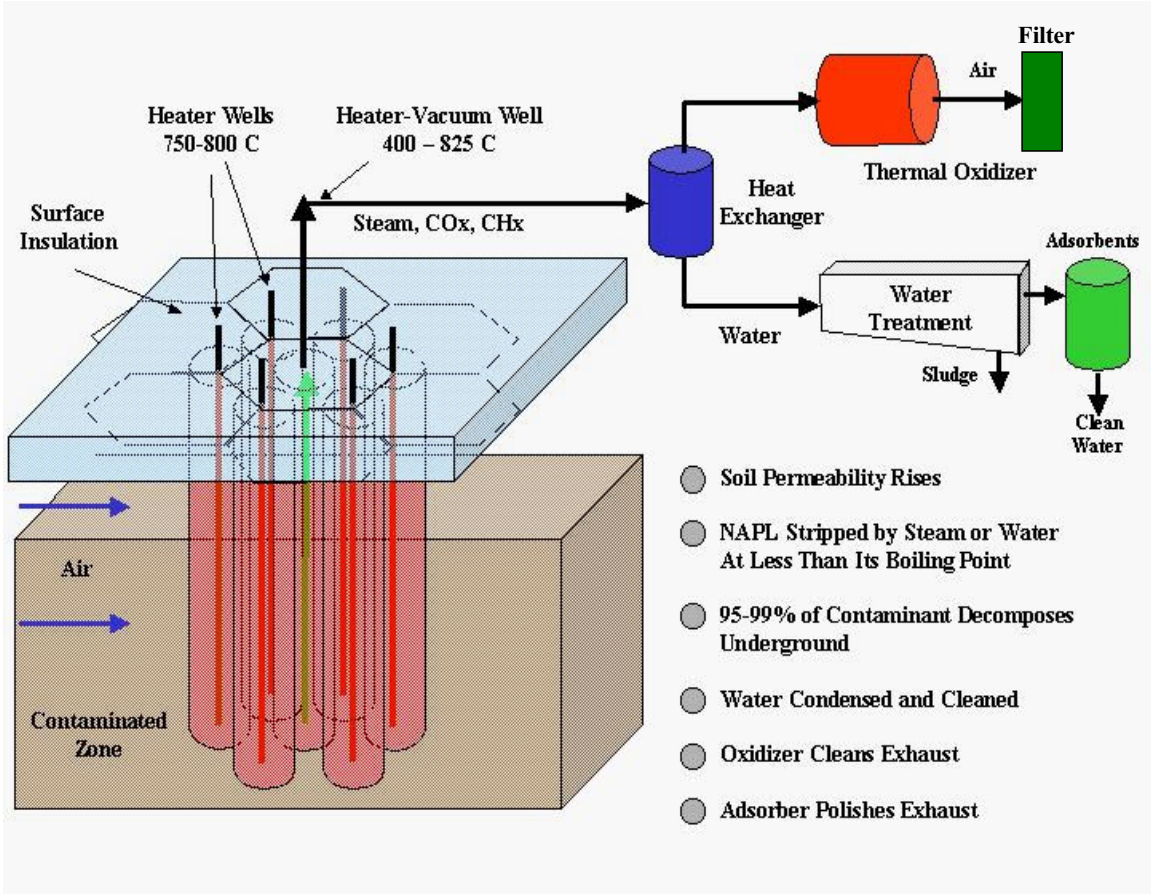

Figure 3. Schematic of ISTD process.

The ISTD process can effectively destroy nitrate salt as a potential oxidizer at temperatures above 310°C (590°F). Reactivity studies have been done on surrogate and waste salt. Heating past the eutectic melting point of salt (210 to 250°C [410 to 482°F]) to decomposition (270 to 310°C [518 to 590°F]) effectively destroys sodium nitrate and potassium nitrate, which are potential oxidizers. However, if sufficient nitrates are present in intimate contact with finely divided reducing material such as carbon, reactions may be induced before decomposition is complete.

In situ thermal desorption can be done at a range of treatment-zone temperatures (TerraTherm 2005a). Lower treatment-zone temperatures (100 to 200°C [212 to 392°F]) are appropriate for removing VOCs and water; this is the temperature range of interest for the SDA. Higher treatment-zone temperatures (greater than 200°C [392°F]) are used for removing and destroying semivolatile compounds. Treatment-zone temperatures of 400 to 500°C (752 to 932°F) have been used to remove and destroy polychlorinated biphenyls at some field sites (TerraTherm 2005b; TerraTherm 2005c; U.S. Navy 1997). Spacing of boreholes and operating temperature of heaters depend on the nature of the contamination, the rate of removal desired, the physical properties of soil or waste to be treated, and the compounds targeted for treatment.

The ISTD system was designed for organic contaminated soil but can be used on buried debris. During the ISTD process, buried waste is heated to cause chemical and physical changes both in the matrix and the contaminants. Organics are volatilized or decompose. Nonvolatile metals and radionuclides may remain unchanged or partition into new or altered phases of soil and waste during

treatment. Though the primary purpose of ISTD is to destroy organic contaminants, any retardation of actinide leaching is desirable.

In this study, ISTD has been evaluated at four temperatures: 20, 105, 275, and 450°C (68, 221, 527, and 842°F). At low temperatures, this technique has the potential to remove significant quantities of volatile and semivolatile organics. At higher temperatures, this technique has potential to degrade nitrate salt and some organic compounds and possibly remove them completely. The testing focused on criteria specific to the SDA application, such as release of acid gases, interaction of nitrate salts and organics, and fixation of actinides on soil or waste, as a result of heating to demonstrate effectiveness.

2.2 In Situ Grouting

In situ grouting is being considered for treatment of TRU pits and trenches, ISTD pretreated TRU pits and trenches, and non-TRU pits and trenches and soil vault rows. Jet grouting is the specific ISG technique being considered for buried waste within the SDA. Jet grouting uses a specially designed rotary-percussion drill rig to deliver and intimately mix grout with soil, debris, and contaminants in the subsurface (see Figure 4). For purposes of this report, ISG will refer to jet grouting. The grout is injected at approximately 6,000 psi through small nozzles; the high pressure, combined with the dense grout, provides the energy required to mix the grout and subsurface materials.

Information gathered in previous testing (Loomis et al. 2003) indicates that the jet-grouting process will not always cut through a waste drum.[f] The jet-grouting process, therefore, is accomplished on a 51-cm (20-in.) triangular pitch matrix, which guarantees that each 55-gal drum will be punctured and filled with as much grout as the voids in the drum will allow (see Figure 5). In addition, with that matrix, each large box will be punctured with multiple applications of grout. Each injection of grout in homogenous soil forms a column, and a series of diagonally offset and connected columns forms a monolith (Loomis et al. 2003). Testing in the field has shown these jet-grouted monoliths to be regions with intimately mixed grout and waste, the spacing of jet-grouting processes resulting in overlapping columns that do not maintain distinct boundaries. The monolith is not homogenous (unless the waste is homogenous in the region the monolith is placed); it is a series of contiguous mixed regions. Overlapping column placement decreases potential for voids in the final monolith and results in a unified mass from a set of discrete injection points. The degree of overlap among columns depends on the injection pressure, grout density, waste density, void space, container form, and debris content.

Grouts must be designed specifically for ISG to meet viscosity, particle size, and set times required for effective operation of the grouting rig. Past bench- and field-scale testing (Loomis et al. 2003) have demonstrated the implementability parameters (Shaw 2004) of the grout formulations being tested, specifically, GMENT-12, U.S. Grout, TECT HG, Saltstone, and WAXFIX. In addition, it is anticipated that the Portland-cement grouts tested will also be able to meet the implementability requirements (e.g., viscosity, particle size, and set times). GMENT-12, U.S. Grout, and TECT HG (proprietary Portland-cement-based formulations); nonproprietary Portland-cement-based formulations; and WAXFIX grout materials have been evaluated to determine the effectiveness of each grout based on leaching and physical characteristics to develop a recommendation for a single material for each application.

f. To cut through a waste drum, the nozzle must be very close to the drum, and the jet must be in contact with the drum long enough to erode or puncture the drum. Corroded metal is easier to cut through than noncorroded metal.

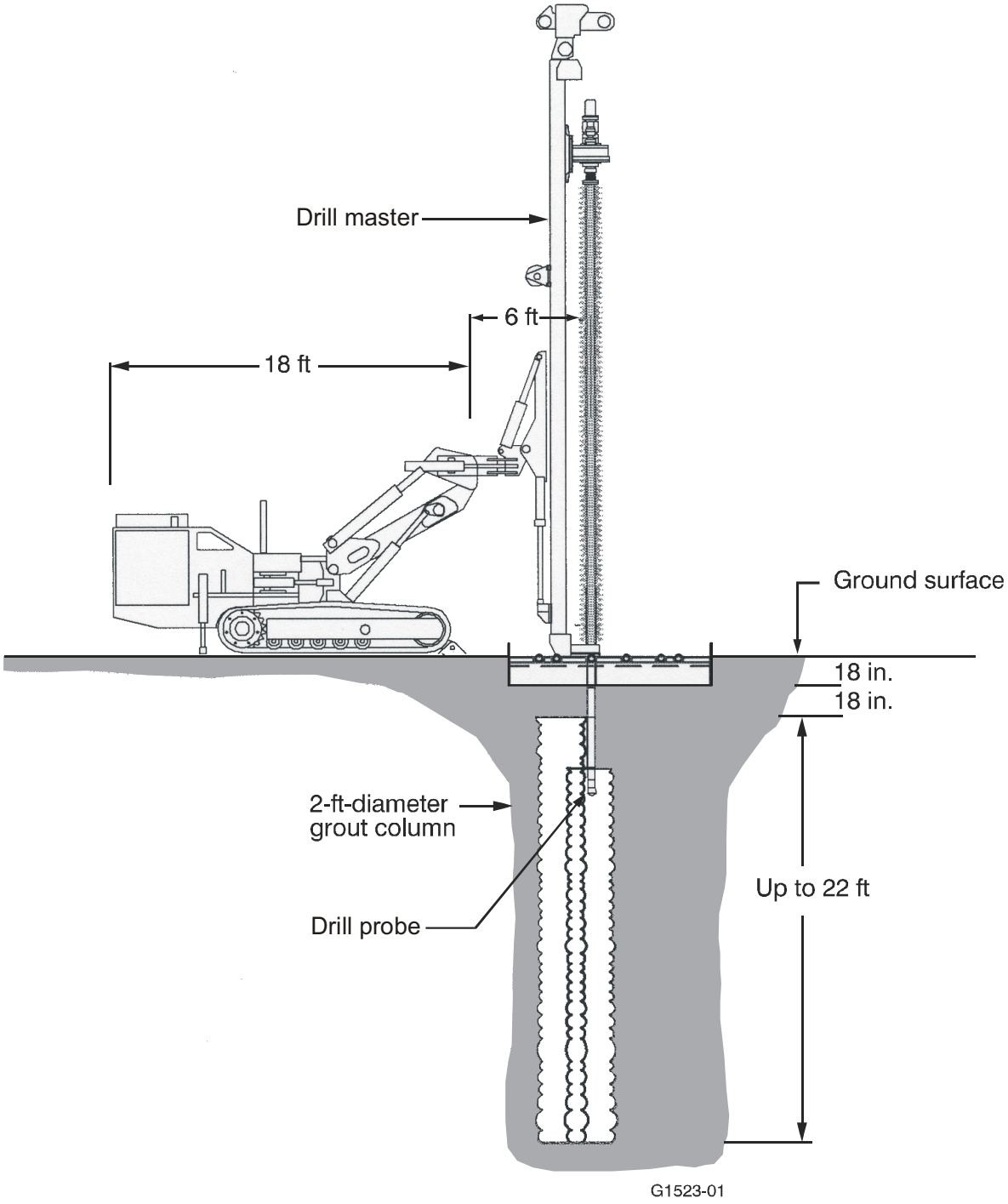

Figure 4. Preconceptual schematic of the overall process of in situ jet grouting.

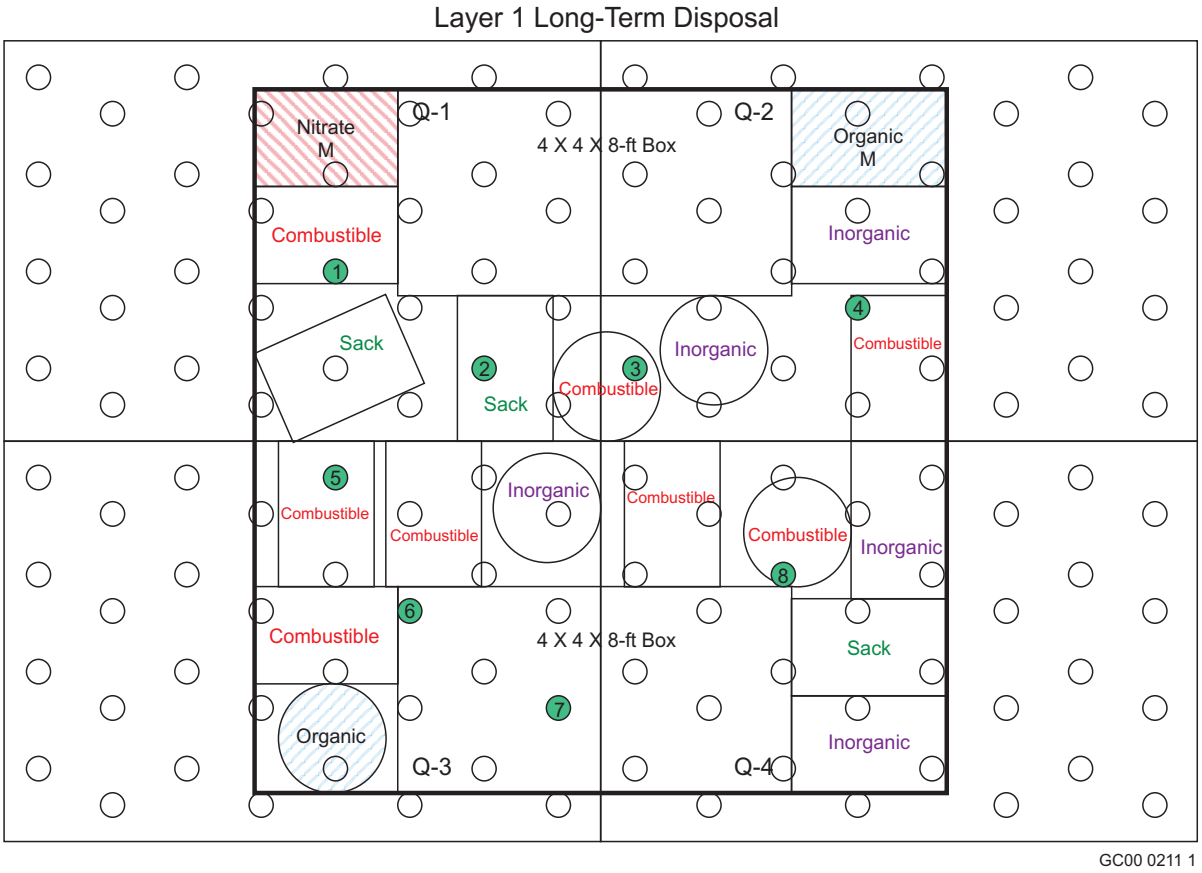

Figure 5. Example of 20-inch, triangular-pitch, jet-grouting pattern.

2.3 Ex Situ Grouting

Ex situ grouting (solidification) is being considered for treatment of the Pad A salt waste. Ex situ grouting includes selection of an appropriate grout and an approach to transfer the waste from Pad A to a mixing system where containers could be opened, waste contents mixed with grout, and grout-waste mixture placed in containers for disposal. Three candidate grouts[g] have been identified for testing: Polysiloxane, Saltstone, and WAXFIX.

3. TESTING

The tests in this report address six main objectives from Yancey et al. (2003):

1. **Develop data to support contaminant transport modeling for treated waste forms.** Data obtained from these tests will be used in modeling migration of contaminants in the final waste form after ISG or ESG. In addition, these data will be used to determine changes in leachability of actinides from the waste and surrounding soil following ISTD heating. These data will support modeling to estimate the release rate of contaminants from the treated waste and compare it to the predicted release rate from untreated waste. The test results also will support risk assessment, the risk model, and evaluation of residual risk for the proposed alternatives for the feasibility study for OU 7-13/14.

g. Dimethyl Polysiloxane, marketed by Technology Visions Group, uses a polymer encapsulation technology (Loomis, Miller, and Prewett 1997) shown to successfully encapsulate surrogate salt materials. Saltstone grout, developed by Savannah River Site, has been developed for salt encapsulation. WAXFIX also is considered in the in situ portion of Yancey et al. (2003).

2. **Evaluate durability of grouted waste.** Physical property data will be obtained to compare grouts and waste loadings. Long-term physical stability of the grouted waste forms will be estimated from these near-term tests.

3. **Evaluate WAXFIX for use as a grout.** The purpose of these tests is to understand better the advantages and limitations of WAXFIX as a grout for TRU and non-TRU waste. The data will be used to address potential criticality and reactivity concerns that may be encountered with specific types and concentrations of contaminants. The ability of WAXFIX to contain radionuclides and nitrates is evaluated. In addition, the generation rate of hydrogen gas for WAXFIX mixed with radionuclides will be assessed because of the radiolysis process.

4. **Quantify major emissions as waste and soil are slowly heated.** Determining primary off-gas constituents and concentrations as waste and soil are heated will help identify the off-gas processing requirements for full-scale test planning. The carbon monoxide and carbon dioxide releases determine the relative amounts of combustion and pyrolysis occurring. The gas proportion measurements also could assist in monitoring the type of waste being heated and any nitrate organic reactions. In addition, these data will support the generation of safety and design data for OU 7-13/14.

5. **Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste.** Quantifying the removal or destruction of chlorinated VOCs and nitrate salt in the waste will help establish anticipated efficiency of ISTD-mediated removal or destruction of COCs in the TRU pits and trenches waste. The data also will be used to generate design data for the pending feasibility study for OU 7-13/14.

6. **Test potential mixtures of organics and nitrates for reactivity.** Determining whether mixtures of nitrate salt sludge and organic sludge will react exothermically during heating by ISTD will help establish temperature ranges to avoid such reactions.

Twenty different tests were performed to address these objectives. Details of the objectives, design, apparatus, procedures, and results for each test are provided in Appendixes B through T of this report. The objectives were developed to assist in evaluation of three technologies—ISTD, ISG, and ESG—being considered for use in remedial alternatives for the SDA. The objectives that are applicable to each technology are shown in Table 1.

4. DATA ANALYSIS AND INTERPRETATION—ISTD

The primary goal at the SDA for ISTD is removal or destruction of organics. The presence of organic contaminants in the SDA is a concern in and of themselves, but they also complicate the grouting process, so removal of organics is of primary concern. The second goal is that the ISTD process be maintained within the established process controls. The third goal is that the ISTD process not mobilize contaminants more than has already occurred.

The discussions that follow cover the four test plan objectives for ISTD:

- Develop data to support contaminant transport modeling for treated waste forms (Section 4.1)
- Quantify major emissions as waste and soil are slowly heated (Section 4.2)
- Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste (Section 4.3)

- Test potential mixtures of organics and nitrates for reactivity (Section 4.4).

This testing includes retrieved waste and surrogates, depending on the type of testing conducted.

Table 1. Applicability of test objective to each technology.

Objectives	Technologies		
	In Situ Thermal Desorption	In Situ Grouting	Ex Situ Grouting
1. Develop data to support contaminant transport modeling for treated waste forms	X	X	X
2. Evaluate durability of grouted waste		X	X
3. Evaluate WAXFIX for use as a grout		X	
4. Quantify major emissions as waste and soil are slowly heated	X		
5. Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste	X		
6. Test potential mixtures of organics and nitrates for reactivity	X		

4.1 Develop Data to Support Contaminant Transport Modeling for Treated Waste Forms

Treatment of surrogate and waste by ISTD does not result in formation of consolidated material (test monoliths) required for American Nuclear Society (ANS) leach testing. Another useful indicator of contaminant mobility is the partition coefficient (K_d). Partition coefficients can be measured on unconsolidated material, such as ISTD-treated material. Estimates of K_d for rare earths and radionuclides were measured for ISTD-treated waste and surrogates. Evaluating the leachability of contaminants using K_d data helps to answer the question of the effects of ISTD on leachability.

4.1.1 Partition Coefficients for ISTD-Treated Nonradioactive Surrogates

Three types of surrogates expected to contain high amounts of TRU contaminants (organic sludge surrogate, inorganic sludge surrogate, and soil) were leach tested. The recipes for surrogates are included in Appendix A. Soil used in testing was from the RWMC area (where waste and soil reside) of the INL Site; it was dry and was sieved for uniformity.

Each of the surrogates was spiked with one or several of four rare-earth elements to simulate radionuclides. Four rare-earth elements were used in testing: terbium, lanthanum, cerium, and neodymium.

4.1.1.1 *Leaching of Surrogate and Soil.*

After heating to simulate ISTD treatment, solid residue from the organic sludge surrogate, inorganic sludge surrogate, and soil was allowed to cool to room temperature. Samples of material, 1 to 10 g (0.04 to 0.35 oz) in mass, were weighed to the nearest milligram and placed in polypropylene bottles. Enough simulated groundwater was added to each bottle so that the liquid-to-solid ratio was 10 mL (0.34 oz) liquid volume to 1 g (0.04 oz) solid mass. Generally, a 10-g (0.35-oz) sample was added to 100 mL (3.38 oz) of simulated groundwater. This extractant is the same pH-8 groundwater simulant used for grout leach testing. This simulated groundwater is prepared in a 50-L (13.2-gal) batch in accordance with the recipe in Table A-1 of Appendix A.

The samples were maintained at room temperature and stirred or shaken for 24 hours to allow for equilibration between the sample and the solution. The K_d is calculated in Equation (1):

$$K_d = [M]_{solid}/[M]_{solution} \quad (1)$$

where:

$[M]_{solid}$ = amount of metal assigned per unit mass of soil in milligram per kilogram

$[M]_{solution}$ = dissolved concentration of metal in equilibrium with the solid in milligram per liter.

In dilute solutions, a plot of $[M]_{solution}$ as a function of $[M]_{solid}$ should be linear. A regression analysis is performed on the plot, and the slope equals K_d. A full K_d analysis was beyond the scope of this work; measurements were taken at a single solid concentration. The data presented in this report provide a first approximation of K_d for the rare earths tested. The units of measure are milliliters per gram.

4.1.1.2 *Soil.*

Measured lanthanum, cerium, and neodymium occurred naturally in the soil, while terbium was added as an oxide to the soil. The K_ds for lanthanum, cerium, and neodymium remained fairly constant as the temperature increased (see Figure 6), while the K_d for terbium appeared to increase as the temperature increased above 275°C (527°F); there was no statistical difference between the four rare earths at 610°C (1,130°F). The mean K_d was on the order of 1E+06 for most of the rare earths and temperatures; the 95% confidence intervals for most of these same data were the same order of magnitude as the mean (see Table K-3 in Appendix K for details). No statistically significant differences exist in the K_ds between ISTD-treated and untreated material or among the rare earths. The results here do not provide any evidence to suggest that thermally treating the surrogate will result in a change in leachability as determined from the K_ds. The general concern here is that thermally treating the waste may alter the state or phase of the contaminant, or it may change the leachability of the contaminant due to a change in the matrix. In this case, we did not look directly at changes in the contaminants' phase or chemical state. The K_d test more generally looked at changes in the leachability, more likely due to changes in the waste matrix.

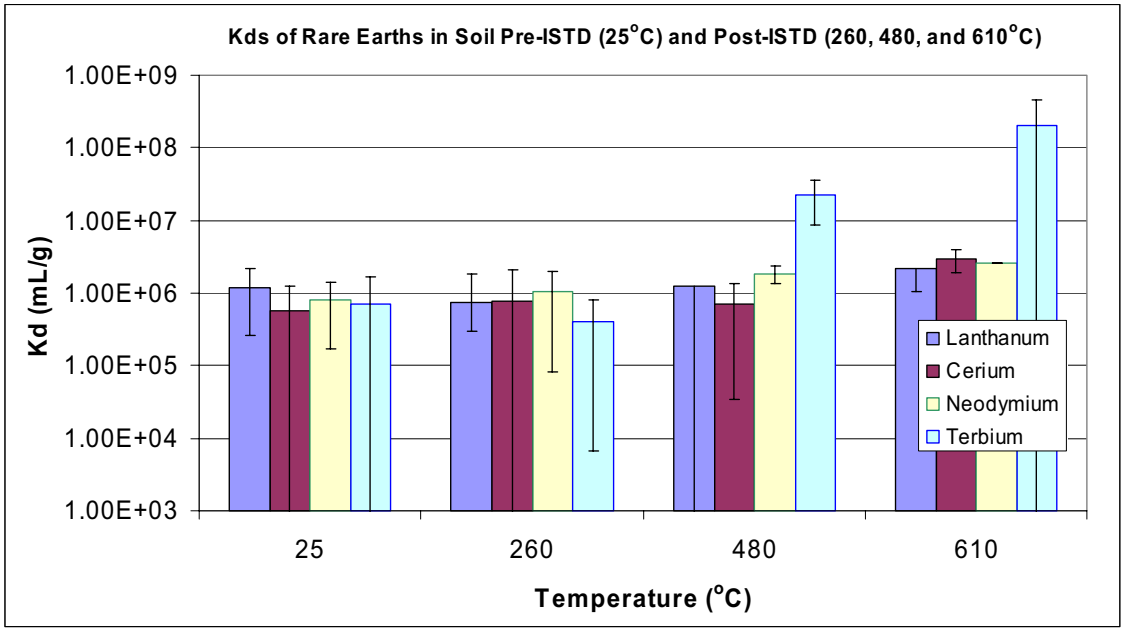

Figure 6. Partition coefficients of rare earths from soil.

4.1.1.3 Inorganic Sludge Surrogate. Lanthanum, cerium, and neodymium, as nitrates, and terbium, as an oxide, were added to the inorganic sludge surrogate. The K_ds for lanthanum, cerium, neodymium, and terbium remained fairly constant as the temperature increased (see Figure 7). The mean K_d was on the order of 1E+06 for most of the rare earths and temperatures; the 95% confidence intervals for these same data were the same order of magnitude as or one order larger than the mean (see Table K-4 in Appendix K for details). No statistically significant differences exist in the K_ds between ISTD-treated and untreated material or among the rare earths. Again, there is no evidence to suggest that thermally treating the waste will result in a decrease in the leachability or mobility of the contaminants tested.

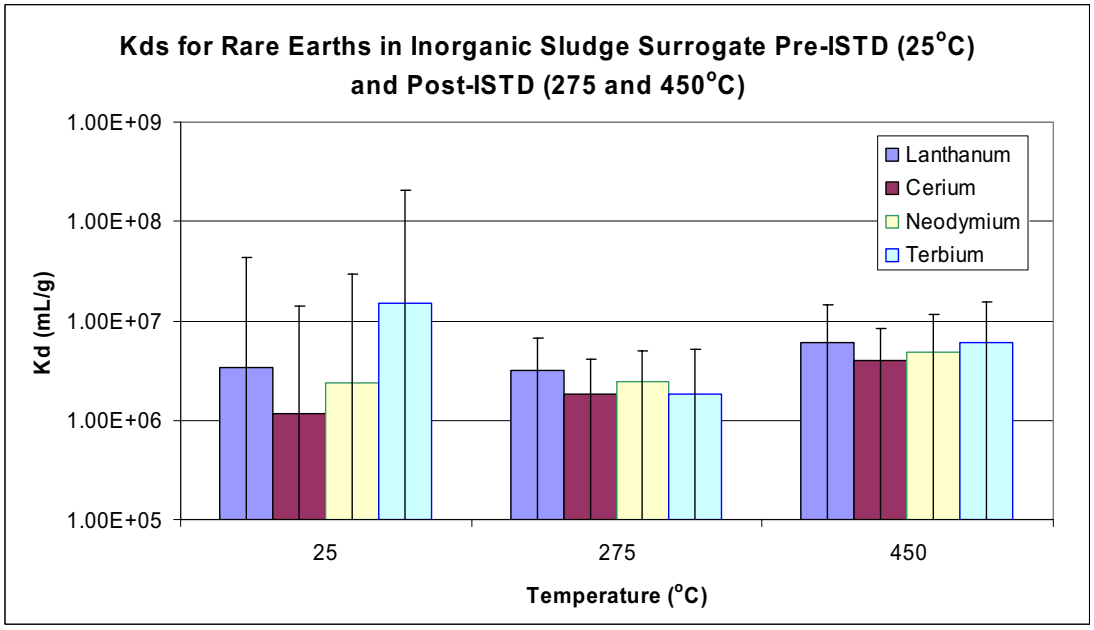

Figure 7. Partition coefficients for rare earths from inorganic sludge surrogate.

4.1.1.4 Organic Sludge Surrogate. Lanthium, cerium, and neodymium, as nitrates, and terbium, as an oxide, were added to the organic sludge surrogate. The K_ds for lanthanum, cerium, neodymium, and terbium appear to increase as the temperature increases (see Figure 8; error bars are not present for the 25 and 105°C (77 and 221°F) data because no replicates were taken for these points); however the 95% confidence interval for each of the rare earths at 650°C (1,202°F) exceeds the value of the mean. The mean K_ds spanned seven orders of magnitude: 1E+02 to 1E+09. The values of the 95% confidence intervals for these same data were the same order of magnitude or larger than the mean (see Table K-5 in Appendix K for details). Because of the high degree of variance, no statistically significant differences could be determined in the K_ds between ISTD-treated and untreated material, among rare earths or temperatures.

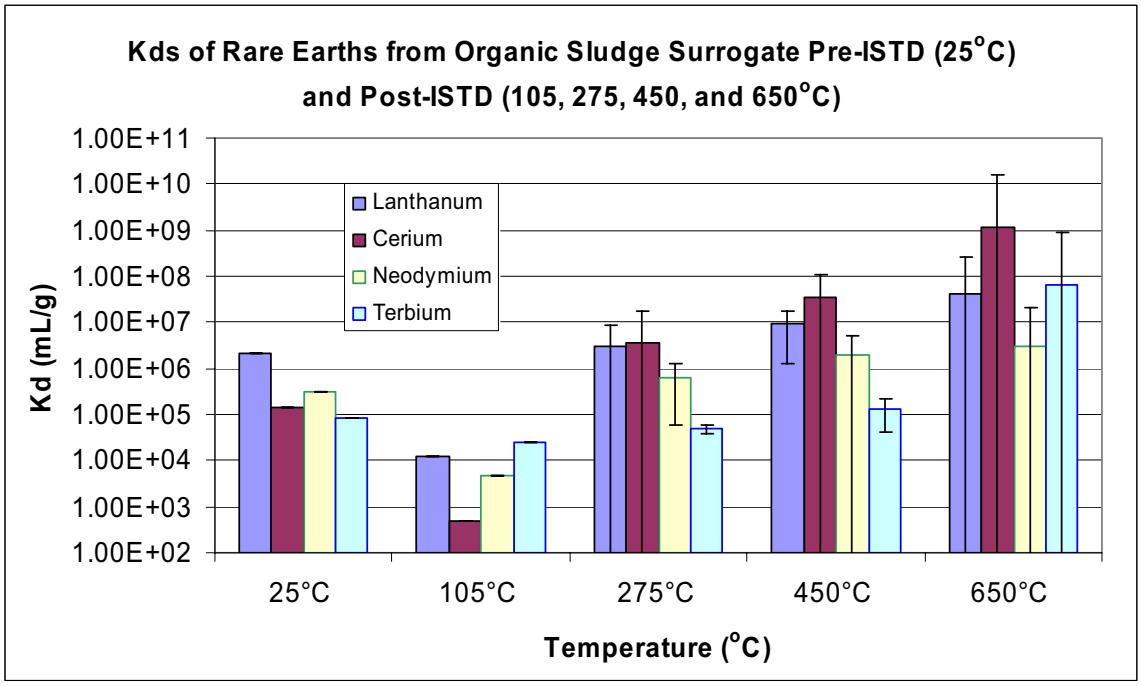

Figure 8. Partition coefficients for rare earths from organic sludge surrogate.

4.1.2 Partition Coefficients for ISTD-Treated Transuranic Surrogates and Waste

For soil from the INL Site spiked with radionuclides (americium, uranium, plutonium, and neptunium) and then processed by ISTD, the K_ds for americium, uranium, plutonium, and neptunium did not change significantly (compared to pre-ISTD) with temperature, except for neptunium at 450°C (842°F), where the K_d increased (see Figure 9). When radionuclides were tested, there was no benefit from the standpoint of decreasing leachability when the waste was thermally treated. The only exception is with americium, where there was an increased K_d for ISTD treatment at 450°C (842°F) compared to no ISTD. The results were statistically different at the 95% confidence interval.

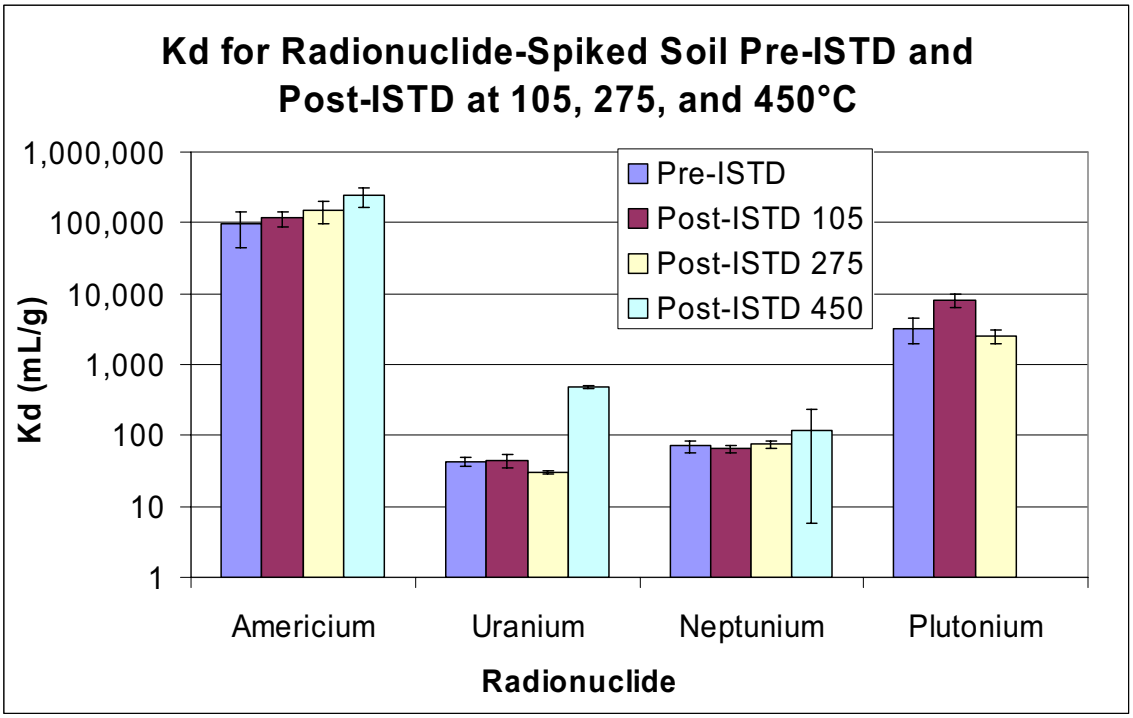

Figure 9. Partition coefficient for radionuclide-spiked soil pre-ISTD and post-ISTD at three temperatures.

For radionuclide-spiked inorganic sludge surrogate, the K_ds for americium and plutonium did not change with temperature (see Figure 10), suggesting that ISTD has no effect on the mobility of americium and plutonium. The K_ds for uranium were statistically higher (confidence interval) from pre-ISTD for 275 and 450°C (527 and 842°F), but there was no statistical significant difference between 275 and 450°C (527 and 842°F). This suggests that ISTD may reduce the mobility of uranium in inorganic sludge. The K_ds for neptunium at 275 and 450°C (527 and 842°F) were statistically lower (confidence interval) than for pre-ISTD, and the K_d at 450°C (842°F) was statistically lower than the K_d at 275°C (527°F). This suggests that ISTD may increase the mobility of neptunium in inorganic sludge. The reason for the difference in behavior among the four radionuclides is not known. Given the uncertainty in much of the data, only preliminary conclusions should be drawn from these results.

The K_d measurements shown in Figure 11 reveal that organic sludge surrogate partitioned similarly to the organic waste. Partition coefficients for uranium and plutonium were lower for the surrogate than for the waste pre-ISTD. Given the aging that could have occurred in the organic sludge waste, the uranium and plutonium in the surrogate could be more mobile than in the waste. Heating both the surrogate and waste sludge during ISTD treatment appears to have resulted in a less-leachable matrix, except possibly for americium; however, caution is advised in interpreting the results. The 95% confidence intervals were of the same magnitude as the mean for several data points. In addition, all metal concentrations in the aqueous phase were low. Small percent variances in these results near detection limit lead to large changes in K_d.

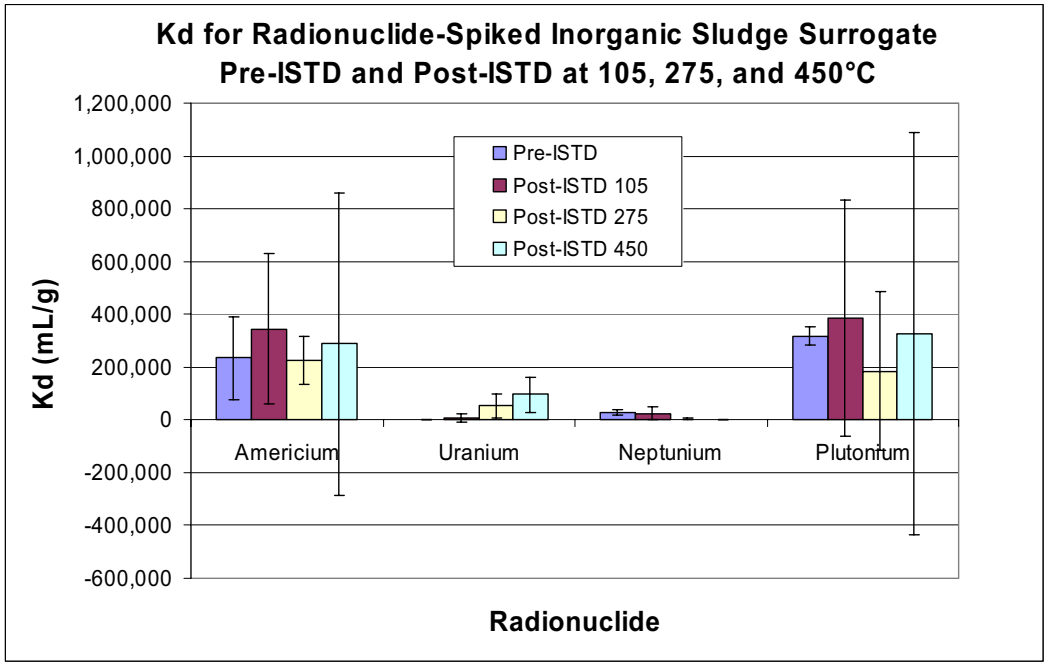

Figure 10. Partition coefficient for radionuclide-spiked inorganic sludge surrogate pre-ISTD (20°C [68°F]) and post-ISTD at three temperatures.

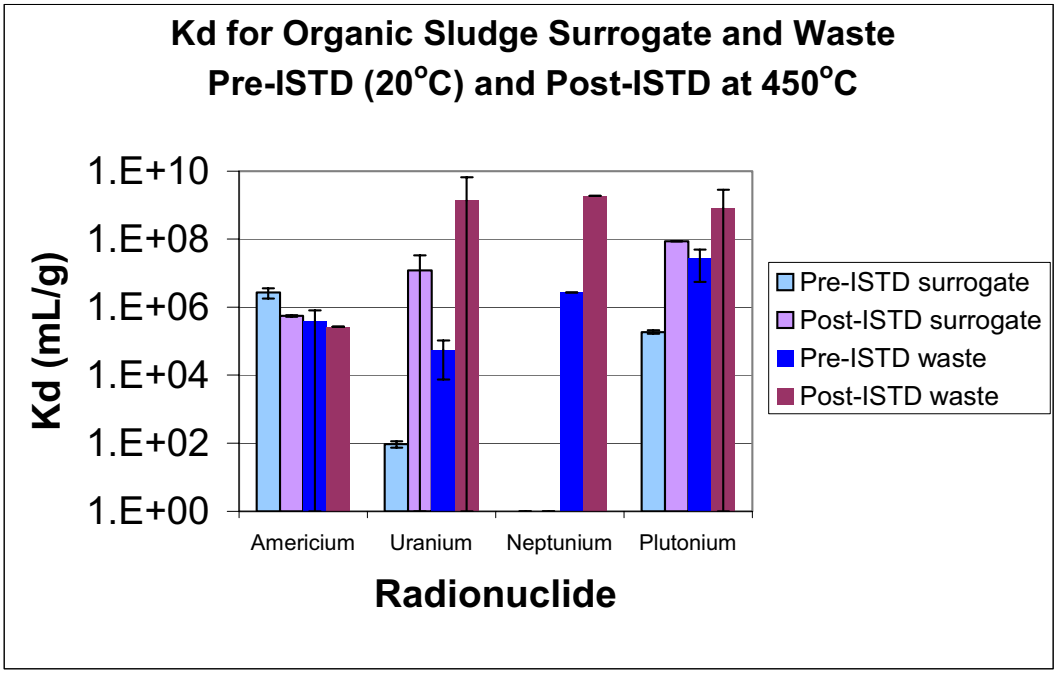

Figure 11. Partition coefficients for radionuclides in organic sludge surrogate (no neptunium added) and organic sludge waste pre-ISTD (20°C [68°F]) and post-ISTD (450°C [842°F]).

4.1.3 Conclusions for Contaminant Transport Modeling for ISTD

No clear pattern emerged from the K_d data for ISTD-treated surrogates and waste at the temperatures studied. In soil, only the K_d for neptunium showed an increase (significant at 95% confidence level) at an ISTD temperature of 450°C (842°F) compared to pre-ISTD. For inorganic sludge surrogate, the K_ds for uranium were higher (at 95% confidence level) than for pre-ISTD for 275 and 450°C (527 and 842°F), and the K_ds for neptunium at 275 and 450°C (527 and 842°F) were statistically lower (95% confidence level) than for pre-ISTD, meaning that the leachability of neptunium increased following ISTD treatment. For the organic sludge surrogate and waste, ISTD treatment appears to have resulted in a less-leachable matrix, except possibly for americium. Caution should be used in interpreting these results; all metal concentrations in the aqueous phase were low, and small percent variances in these results near detection limit lead to large changes in K_d.

One of the parameters tested for ISTD treated material was the ability of ISTD to reduce the leachability of the radionuclide COCs from the specific matrices. The results from this study do not provide evidence to show that this occurs. Only in the case of high-temperature ISTD of organic sludge does ISTD appear to provide a benefit by reducing leachability of radionuclides with the exception of americium. For soil from the INL Site and inorganic sludge, the leachability of the contaminant was usually unaffected as a result of the ISTD treatment, even at high temperatures.

4.2 Quantify Major Emissions as Waste and Soil are Slowly Heated

Surrogates (with and without radionuclides) and waste were used for tests in this section, as noted. The overall objective of this work was to better quantify the type of emissions that could be released during ISTD. Section 4.2.1 covers the work completed by MSE on nonradioactive surrogates. The MSE tests were larger drum-scale tests. Section 4.2.2 covers the ISTD of radioactive surrogate and waste completed at the INL Site, and was performed on a smaller scale using surrogate and waste that was ISTD treated. The second set of tests was used to confirm that the MSE drum-scale tests matched what would occur using the radioactive waste and surrogate.

4.2.1 MSE Drum Tests

The MSE vacuum thermal desorption system consists of a carbon-steel chamber sized to completely enclose a 55-gal test drum (see Appendix I for details of the equipment). For these tests, the system was operated under a slight vacuum (10.2 to 12.7 cm [4 to 5 in.] of water). The slight vacuum primarily was intended to simulate ISTD heating but also ensured that any gases released in the drum during thermal desorption were drawn into the off-gas treatment system, preventing leakage into the work area around the test bed.

To simulate airflow through soil into the slight vacuum of an ISTD heater assembly, air is metered by a mass flow control valve into the bottom of the 55-gal test drum where the air can be dispersed circumferentially around the drum by a distribution ring or injected at a point near the bottom of the drum. Six thermocouples monitored the temperature of the drum contents during heating: two near the center heater assembly, two halfway between the heater assembly and the drum wall, and two near the drum wall. The thermocouples are identified by position as top or bottom, and inner, middle, or outer.

A shakedown and four surrogate tests were conducted: organic sludge surrogate (Drum 1), nitrate salt surrogate (Drum 2), organic sludge surrogate with combustible debris surrogate (Drum 3), and organic sludge surrogate with combustible debris and soil (Drum 4). All of the tests were conducted with surrogate without radionuclides.

Because the temperature of the drum contents determined volatilization and pyrolysis of drum contents, the primary variable of interest for the ISTD drum tests was the temperature of the drum contents as a function of time. Temperatures of drum contents for the shakedown and the organic sludge, nitrate salt, and organic with combustibles tests are shown in Figure 12. Each line color in the graph indicates a particular test (e.g., green indicates the nitrate salt test [Drum 2]). The legend indicates the test and thermocouple locations as follows:

- The first two or three characters indicate the test: shakedown (Shk), organic sludge (Org), nitrate salt (Nit), organics with combustibles (D3), or organics with combustibles and soil (D4)
- The middle character indicates the thermocouple identifier
- The last two characters indicate the thermocouple locations, which were inner bottom (IB), inner top (IT), midbottom (MB), midtop (MT), outer bottom (OB), and outer top (OT).

As shown in Figure 12, heating rates and maximum temperatures varied substantially from test to test. Factors affecting heating rate were assumed to be power input to the heater, water content in the feed material, airflow into the drum, and fuel value of material volatilizing from the feed.

4.2.1.1 Shakedown Test. The objective of the shakedown test was to check out system components and to monitor the heating profile of the drum contents. The drum contents were a mixture of soil from the INL Site, kitty litter, Microcel E, and water, formulated to simulate the heat capacity, heat of vaporization, and total gas generation of the organic sludge. By using relatively inert constituents, a comparison of the shakedown test to the later organic sludge test (Drum 1) was expected to reveal any heating effects because of organic sludge chemical reactions. The details of the shakedown feed formulation are provided in Table I-2 of Appendix I.

The shakedown feed material was loaded into a 55-gal drum, which was then placed in the main test chamber of the barrel thermal desorption skid. For the shakedown test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

4.2.1.2 Organic Sludge Surrogate Test (Drum 1). The organic sludge surrogate was a mixture of cutting oil, halogenated solvents, and adsorbents; a detailed recipe is provided in Table I-3 of Appendix I. All organic liquids in this surrogate have fuel value. Therefore, this mixture had the potential to react with injected air and produce heat. This combustion process, if it occurred, was expected to take place either within the heater assembly or in the hottest portion of feed material near the heater assembly. For the organic sludge test, electrical power was applied to the heater assembly for 22 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

Off-gas from the organic sludge test was sampled and analyzed for hydrogen chloride and chlorine gas (hydrochloric acid/chlorine) and the four VOCs included in the drum contents. As shown in Figure 13, the peak hydrochloric acid concentration, approximately 33 vol%, was reached 22 hours from the start of the test. Up to that time, there were no detectable feed VOCs in the off-gas. At 18 hours, when drum contents near the drum wall exceeded the target temperature of 105°C (221°F), the heater assembly was powered down. At 19 hours, combustion air to the drum was discontinued. Shortly after at 22 hours, the temperature of the drum contents began to decline, off-gas hydrochloric acid concentrations abruptly dropped off, and off-gas VOC concentrations abruptly increased. The VOC concentrations peaked at about 32 hours from the start of the test. At 35 hours, a nitrogen purge of the drum was started, which resulted in a dilution of the off-gas organics, as reflected in Figure 13.

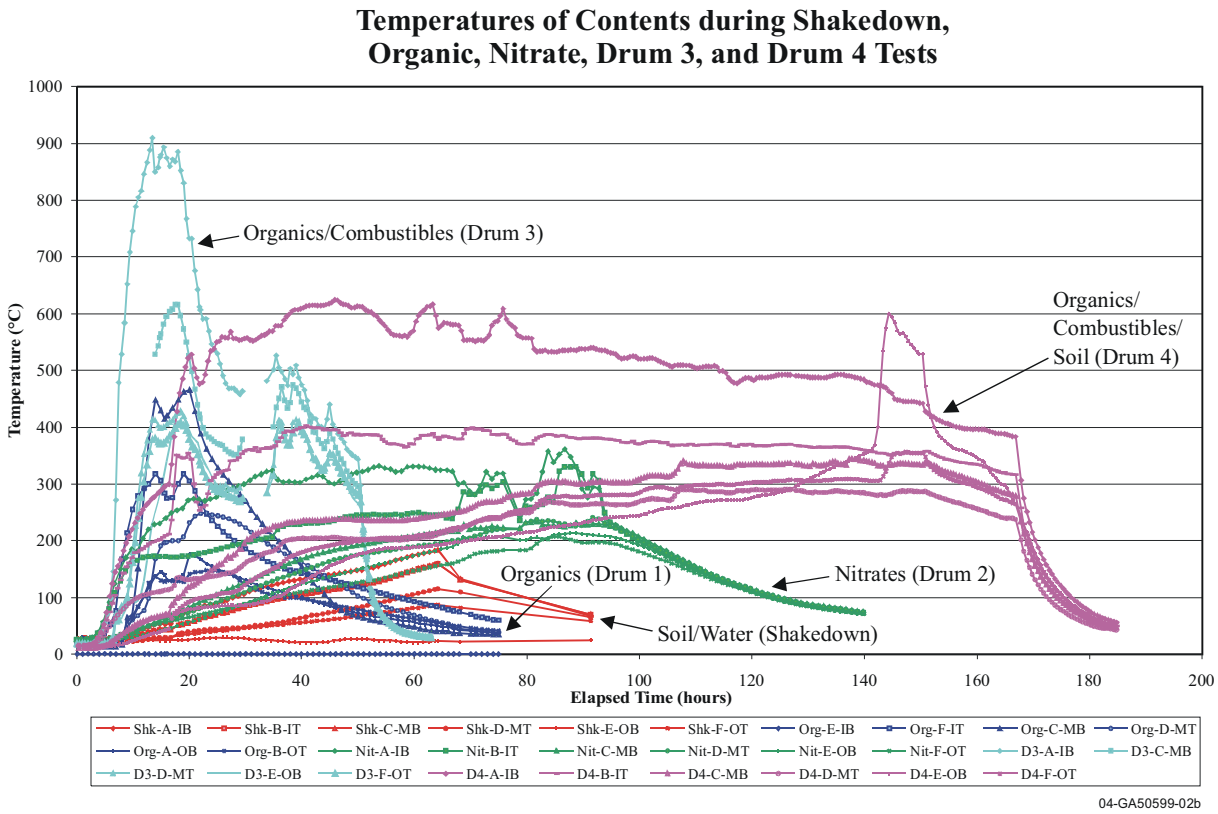

Figure 12. Temperatures of test drum contents.

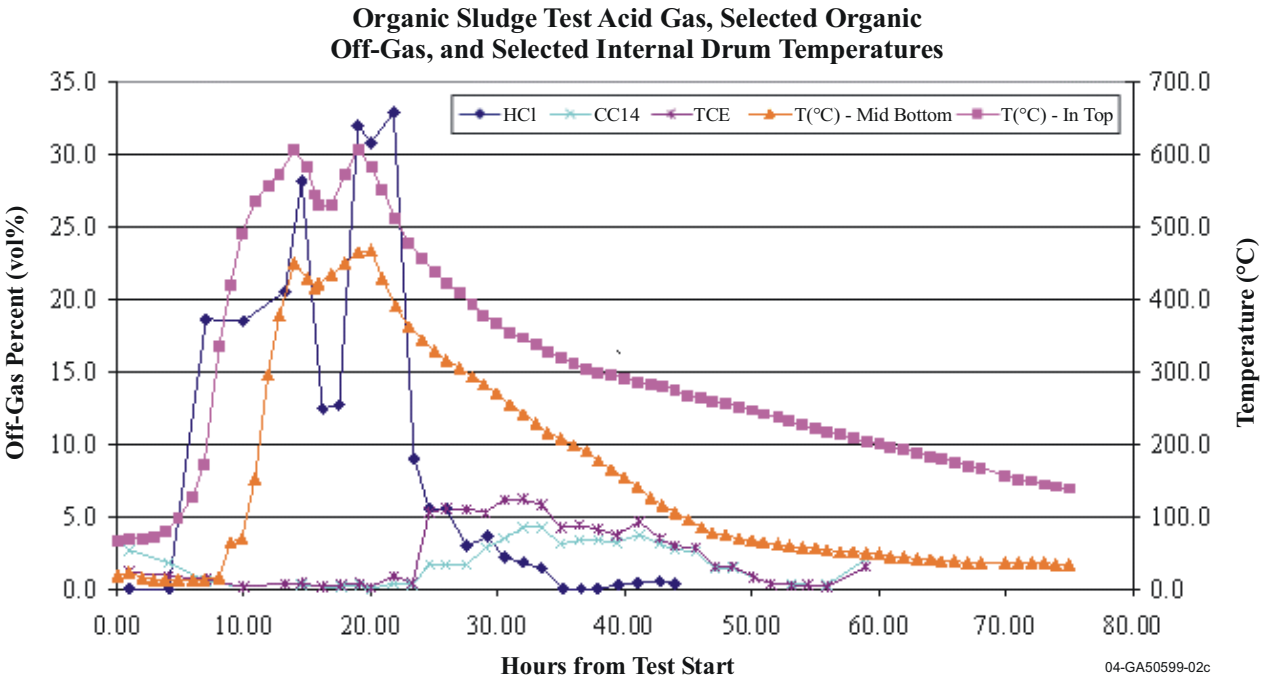

Figure 13. Generation of acid gas in organic sludge test, selected off-gas volatile organics, and selected internal drum temperatures (Drum 1).

The crossover of hydrochloric acid and VOC concentrations apparently was because of incomplete combustion of VOCs volatilized from the feed material. While power was supplied to the heater, the VOCs, which were the only source of chlorine, were evidently fully oxidized to hydrochloric acid, carbon dioxide, and water. When the heater power was turned off, the VOCs continued to volatilize from the drum; however, the presumed combustion zone near or within the heater assembly was apparently no longer hot enough to oxidize the VOCs. A qualitative organic compound scan of an off-gas sample taken during this cooling period showed numerous partially dechlorinated products of the feed organic VOCs, further suggesting incomplete oxidation of organics after the heater power was turned off.

4.2.1.3 Nitrate Salt Surrogate Test (Drum 2). The nitrate salt surrogate was a mixture of 90 wt% nitrate salts, miscellaneous other salts, 1 wt% ethylenediaminetetraacetic acid (EDTA), and 0.5 wt% ceric oxide (added as a plutonium surrogate); details of the recipe are shown in Table I-4 in Appendix I. (The as-mixed formula was normalized to a total of 100%.) For the nitrate salt test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

While the nitrate compounds are strong oxidizers, particularly when heated, the only combustible compound in the mixture was EDTA (at 1 wt%), which provided only a trace of fuel for the nitrate oxidizers. Accordingly, heating this mixture was expected to result in only minimal exothermic reactions. As shown in Figure 12, the heating rate for the nitrate salt drum contents was slightly faster than for the shakedown test and much slower than for the organic sludge surrogate test (Drum 1). For the nitrate salt test, heater power was applied for approximately 65 hours, at which time the temperature of the drum contents peaked at approximately 185°C (365°F). The off-gas was sampled and analyzed for the four VOC compounds of the organic sludge surrogate and for hydrochloric acid/chlorine. As expected, since the feed did not contain VOCs, VOCs were not detected in the off-gas. The feed material contained a relatively minor source of chlorine (3 wt% sodium chloride); however, hydrochloric acid/chlorine also was not detectable in the off-gas, most likely because the temperatures were not sufficient to decompose sodium chloride.

4.2.1.4 Organic Sludge Surrogate with Combustible Debris Test Surrogate (Drum 3). A combustible debris surrogate consisting of 40 wt% cotton rags, 40 wt% paper towels, 10 wt% polyethylene beads, 5 wt% polyvinyl chloride beads, and 5 wt% acrylonitrile-butadiene-styrenes plastic beads was prepared for this test (for additional detail, see Table I-5 in Appendix I). The feed formulation for this test consisted of 35 wt% organic sludge, 55 wt% combustible debris, and 10 wt% water. This formulation was intended to simulate the contents of drums buried at the RWMC that contain cutting oil, halogenated solvents, adsorbents, paper, cloth, and plastic scrap. For the organic sludge with combustible debris test (Drum 3), electrical power was applied to the heater assembly for 50.1 hours. Nominal airflow to the test drum was 0.23 kg (0.5 lb)/minute.

As shown in Figure 12, the peak temperature for the organic sludge with combustible debris drum contents was 910°C (1,670°F), observed at 13.5 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and times for the middle and outer thermocouples were 617°C (1,142.6°F) at 18 hours and 423°C (793.4°F) at 18.5 hours, respectively. Both the rate of temperature rise and the peak temperatures were substantially greater than the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2). Similarly to the organic sludge test, the rapid rise in temperature apparently was because of combustion of the drum contents.

The Drum 3 organics with combustibles feedstock included the organic sludge surrogate (with halogenated solvents) at about one-third the concentration of the test of Drum 1 organic sludge. Consequently, the test of Drum 3 would be expected to show a pattern of off-gas hydrochloric acid and volatile organic generation similar to Drum 1. Drum 3 off-gas hydrochloric acid and volatile organics are shown in Figures 14 and 15, respectively.

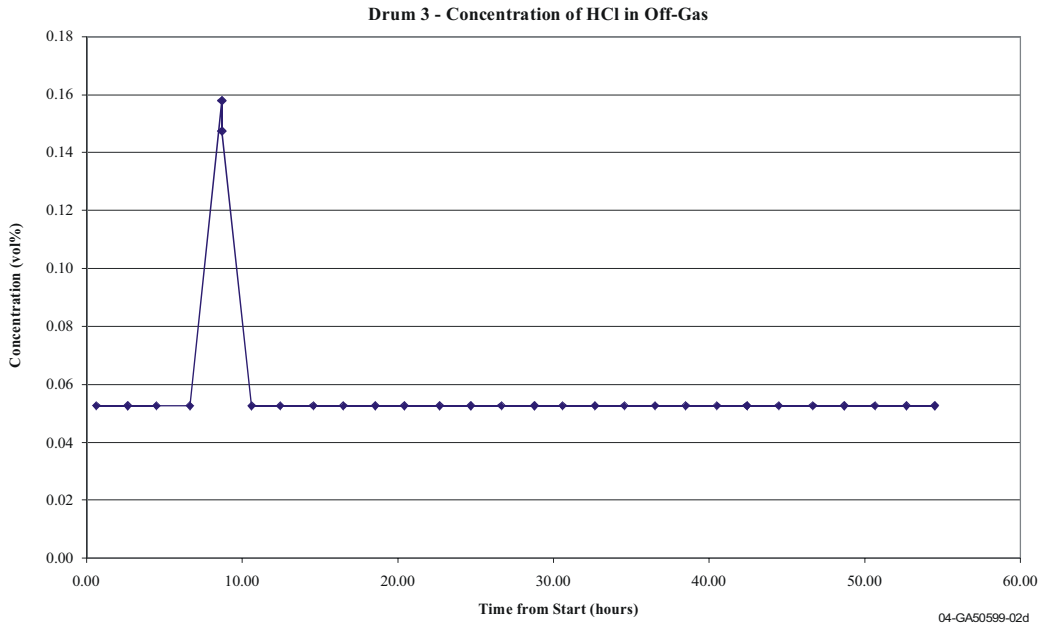

Figure 14. Off-gas hydrochloric acid observed during the test of Drum 3 organic sludge and combustible debris.

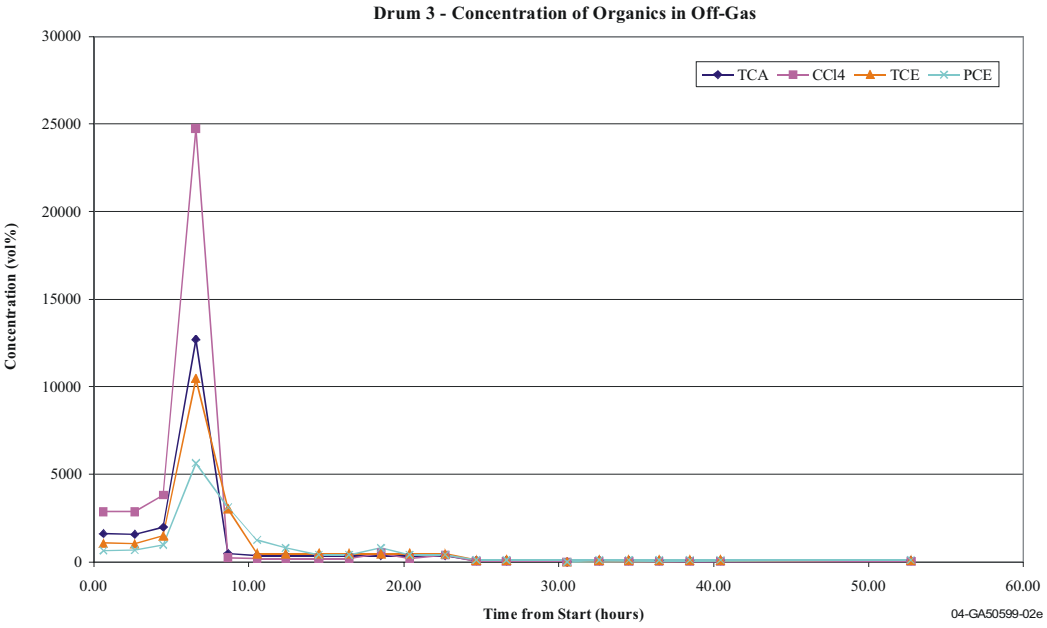

Figure 15. Off-gas volatile organic solvents observed during the test of Drum 3 organic sludge and combustible debris.

Comparison of the Drum 3 results (see Figures 14 and 15) to the Drum 1 results (see Figure 13) indicates much lower off-gas hydrochloric acid and volatile organic concentrations. The Drum 1 results were explained as combustion of halogenated solvents to hydrochloric acid (and carbon dioxide and water) during the early part of the test and volatilization, but poor combustion during the later part of the test. Following this reasoning, the Drum 3 off-gas should show either high concentrations of hydrochloric acid during good combustion or elevated concentrations of volatile organics during poor combustion. Since drum content temperatures were high during the Drum 3 test, the feed halogenated solvents must have volatilized, raising the question of what happened to the chlorine in the halogenated solvents. It appears to have neither burned to hydrochloric acid nor come off unaltered as volatile organics.

Possible alternative fates of feed chlorine are that hydrochloric acid was scrubbed by feed constituents, which seems unlikely since there were no alkaline components in the Drum 3 feedstock or that the halogenated solvents partially pyrolyzed, and the chlorine in the halogenated solvents came off as chlorinated organic combustion products. Rapid heating of the Drum 3 contents may have resulted in incomplete combustion, or the rapid heating and associated evident burning of combustible debris may have caused an off-gas dilution effect caused by rapid generation of large volumes of off-gas.

4.2.1.5 Organic Sludge Surrogate with Combustible Debris and Soil Surrogates Test (Drum 4). A soil surrogate—containing a tracer—consisting of 83 wt% soil from the INL Site, 15 wt% water, and 2 wt% ceric oxide was prepared for this test (additional detail is provided in Table I-6 of Appendix I). The feed formulation for this test consisted of 40 wt% organic sludge, 30 wt% tracer containing soil, and 30 wt% combustible debris. This formula simulated the contents of drums buried at the RWMC mixed with soil from the INL Site. For the organic sludge with combustible debris and soil test (Drum 4), electrical power was applied to the heater assembly for 167 hours. Nominal airflow to the test drum was 0.23 kg (0.5 lb)/minute.

As shown in Figure 12, the peak temperature for the drum contents was 619°C (1,146ºF), observed at 46.8 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and times for the middle and outer thermocouples were 344°C (686ºF) at 138 hours at the middle bottom thermocouple and 600°C (1,112ºF) at 144 hours at the outer bottom thermocouple. Note that the outer bottom thermocouple, and to a lesser extent the outer top thermocouple, showed a spike in temperature near the end of the test. During most of the test, the outer bottom thermocouple registered the lowest temperature of all the drum content thermocouples, as would be expected. However, for approximately 10 hours near the end of the test, the outer bottom thermocouple crossed over and registered the highest temperature in the drum during that period and nearly the highest temperature of any thermocouple for the entire test. Assuming that the high temperature reading was not a malfunction, which seems unlikely since the outer top thermocouple also registered a temperature rise during the same period, the only apparent cause of the temperature spike would have been delayed burnout of drum contents near the outside of the drum.

The peak temperatures for the Drum 4 (see Figure 12) test were greater than for the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2) but less than the test of Drum 3 organic sludge with combustible debris. With the exception of the outer thermocouple temperature spike near the end of the test, the general rate of temperature rise for Drum 4 was less than that observed for all but the shakedown test.

Drum 4 off-gas hydrochloric acid and off-gas halogenated organics are shown in Figures 16 and 17. Comparison of results from Drum 1 (see Figure 13), Drum 3 (see Figures 14 and 15), and Drum 4 shows a closely similar pattern of off-gas hydrochloric acid and halogenated organic evolution for Drum 3 and Drum 4 tests, with both differing substantially from Drum 1, which showed much higher concentrations of off-gas hydrochloric acid and off-gas halogenated organics. The peak hydrochloric acid and halogenated organic concentrations for Drum 4 occurred between 15 and 20 hours from the start of

the test, while peak concentrations for Drum 3 were between 5 and 10 hours from the start of the test. This appears to be consistent with the slower heatup rate for Drum 4, which was expected because of the lower fuel content for Drum 4 feedstock.

Posttest analysis of Drum 4 contents showed very low concentrations of residual halogenated organic feed constituents, generally undetectable, and less than 1 mg/kg in all instances.

Paralleling the discussion of the Drum 3 test results above, the lower concentrations of off-gas hydrochloric acid and halogenated organics for Drum 4 relative to Drum 1 may have been caused by evolution of chlorinated organic pyrolysis products of the Drum 4 feed constituents. To assess this possibility, several off-gas samples from Drum 4 were analyzed using complete mass spectral scans of the sample gas chromatograms. Complete mass spectral scans can reveal and tentatively identify miscellaneous organic compounds in the analysis sample. In this case, analysis of Sample 10, which was taken 16.7 hours from the start of the test, showed relatively high concentrations of partial decomposition products, including benzene, styrene, and several chlorinated organic compounds. Generated over the entire test period, the Drum 4 chlorinated decomposition products might have accounted for the bulk of the chlorine present in the Drum 4 feedstock.

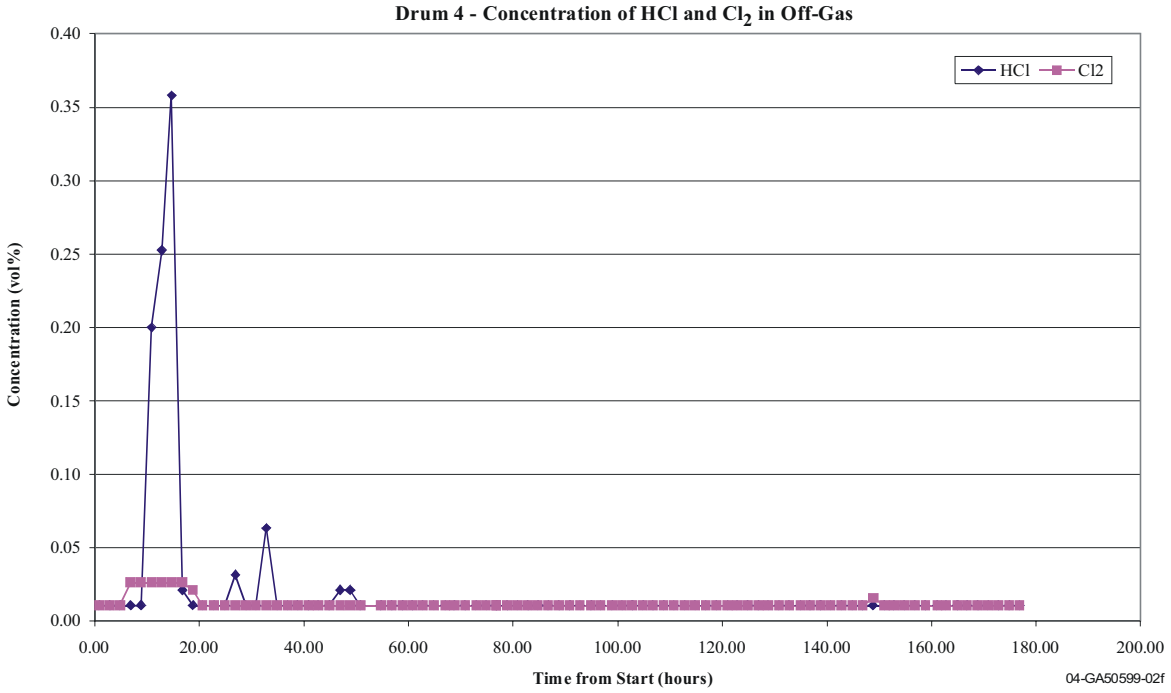

Figure 16. Off-gas hydrochloric acid observed during the test of Drum 4 organic sludge with combustible debris and soil.

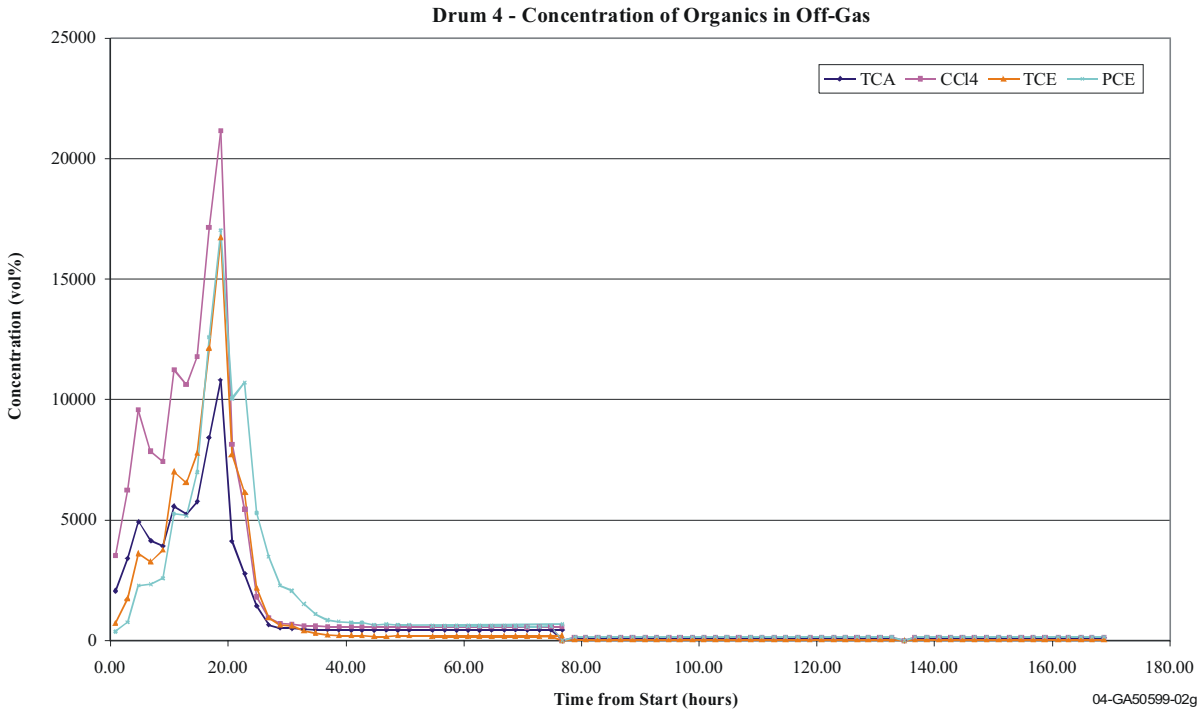

Figure 17. Off-gas volatile organic solvents observed during the test of Drum 4 organic sludge with combustible debris and soil.

4.2.1.6 Conclusions from MSE Drum Tests. Based on MSE tests, oxidation of subsurface materials should be expected if oxygen is present during ISTD. The location and completeness of the oxidation will depend on amount of oxygen present, temperature, and location of oxygen and materials being oxidized. The MSE tests also indicate the potential for chlorinated organic compounds to be released during ISTD. These chlorinated compounds can be readily managed by an off-gas treatment system similar to those regularly employed where ISTD is used to treat organic compounds.

The feedstocks containing significant quantities of combustible materials were essentially self-heating after an initial heatup period, provided that combustion air was supplied to the test drum. The self-heating of combustible drum contents appeared to produce gaseous partial-decomposition products, though supplying electrical power to the heater assembly appeared to be necessary for more complete combustion of the gaseous partial-decomposition products. However, the bulk of the heating power for the drum contents came from combustion of drum contents. The rate of heatup of the drum contents corresponded to the relative amount of fuel in the feedstocks. For these tests, the rate of heating increased in the following order: shakedown (soil and water), Drum 2 (nitrate sludge surrogate), Drum 4 (organic sludge, combustible debris, and soil), Drum 1 (organic sludge), and Drum 3 (organic sludge and combustible debris).

Drum 1 (organic sludge), Drum 3 (organic sludge with combustible debris), and Drum 4 (organic sludge with combustible debris and soil) tests used feedstock containing halogenated solvents. In the Drum 1 test, the off-gas initially contained high concentrations of hydrochloric acid and later relatively high concentrations of feedstock halogenated organics. This was attributed to initial complete combustion of halogenated organics to hydrochloric acid, carbon dioxide, and water, followed by a period of obvious noncombustion of volatilized halogenated organics. The noncombustion of halogenated

organics was apparently caused by removing electrical power from the heater assembly and discontinuing combustion air to the drum, which was done in order to stop the test.

The MSE concluded that the heater assembly performed as expected, gradually heating surrogates of buried organic sludge, nitrate salts, organic sludge with combustible debris, and organic sludge with combustible debris and soil. Heating feedstocks containing halogenated organics resulted in emission of hydrochloric acid, chlorinated decomposition products, and unaltered feed organics, indicating a need for downstream off-gas treatment of buried waste containing high concentrations of organic constituents.

A secondary conclusion was that organic sludge, nitrate salts, and organic sludge with combustible debris could be tested safely in the drum-scale test bed and ultimately treated in this manner in the field. Mixtures of organic sludge or combustible debris with nitrate salts, a combination of fuel and oxidizer, were not tested. Fuel with oxidizer mixtures of this type was tested at the Energetic Materials Research and Testing Center in New Mexico. The results of those tests are reported separately in Section 4.4 and Appendix J of this report.

The results from this test show that heating the waste removes some contaminants from the waste, in particular, the organic fraction and, in some cases, nitrate salts from the waste as long as the temperatures and airflow are controlled. It will be necessary to provide an off-gas treatment system to ensure that contaminants are not released into the atmosphere.

4.2.2 Off-Gas, Bench-Scale Filter, and Mass Balance Analysis during ISTD of Transuranic Surrogates and Waste

These bench-scale tests were conducted using a tube furnace (see Appendixes K and L for a description of the procedures and apparatus).

4.2.2.1 Off-Gas. Grab samples of the off-gas stream were taken periodically (generally at zero, one, and three hours) during ISTD of the organic sludge surrogate, organic sludge waste, and Pad A nitrate salts from a septum port on the line between the filter and the bubbler. These samples were analyzed by gas chromatography-electron capture detector for organochlorine constituents and compared with a carbon tetrachloride gas standard. A split also was analyzed by thermal conductivity detector for carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide. The results are summarized below; the values of individual measurements are provided in Table L-10 of Appendix L.

Organochlorine constituents were analyzed using an electron capture detector. The electron capture detector was calibrated using carbon tetrachloride, and in fact, carbon tetrachloride was detected at very low concentrations (part-per-billion levels) in the off-gas as shown in Figure 18. No significant amounts of carbon tetrachloride were found in the off-gas from the organic sludge waste samples (see Figure 19). Examination of Pad A carbon tetrachloride data in Figure 20 unexpectedly shows small amounts of carbon tetrachloride. Therefore, the carbon tetrachloride concentrations reported here for both waste types may be from residual carbon tetrachloride in the system and not from the samples.

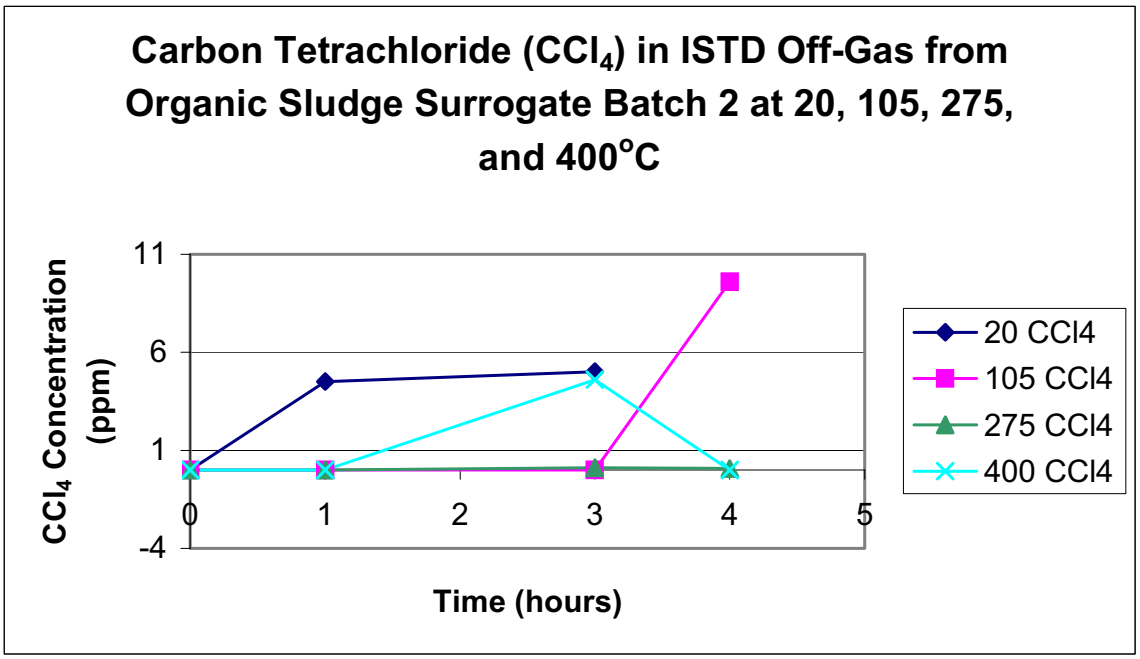

Figure 18. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge surrogate.

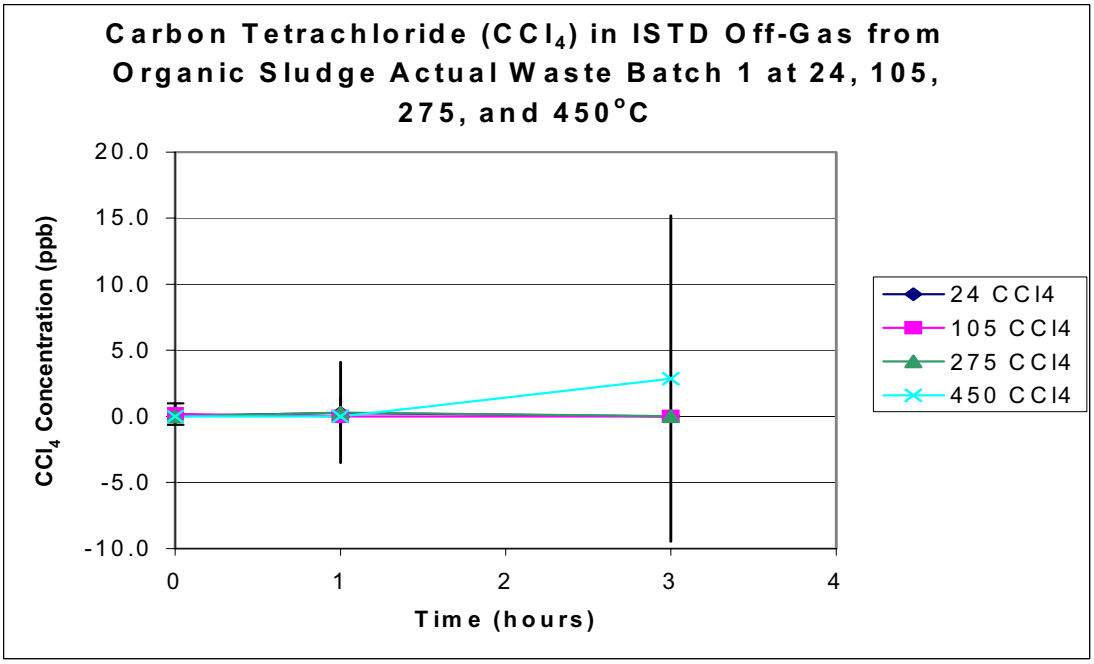

Figure 19. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge waste.

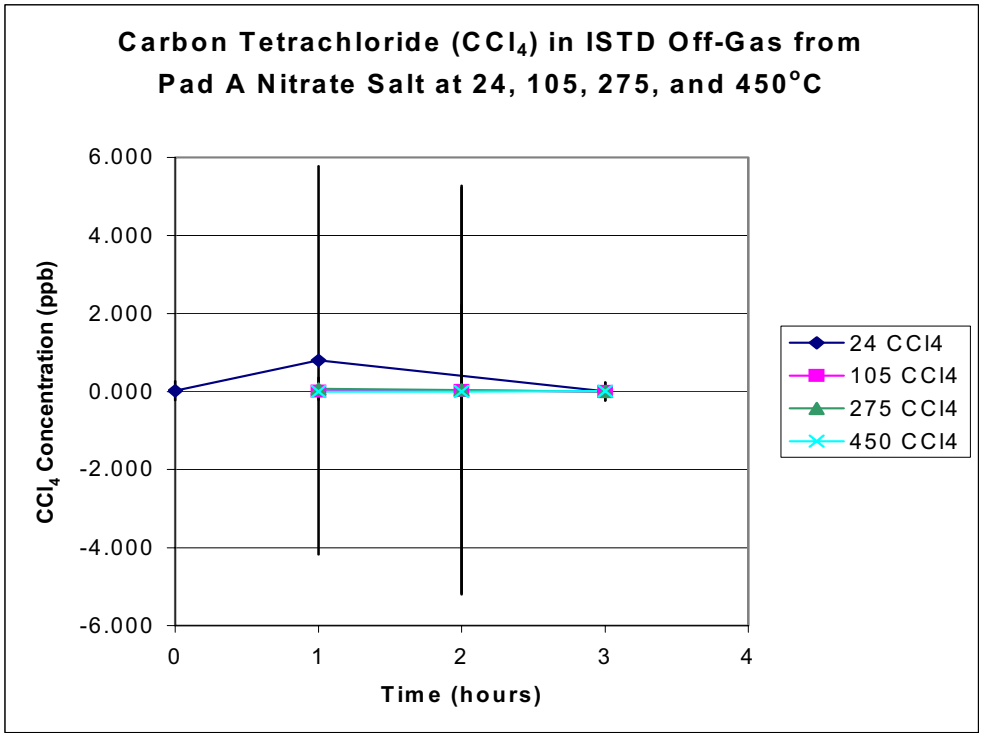

Figure 20. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of Pad A nitrate salt.

Further evidence of this is that no predictable sequence of carbon tetrachloride evolution occurs with time as measurements were made immediately upon achieving temperature for a run (1 hour into the run and 3 hours into the run). This experimental setup may not have been adequate for collecting desired off-gas data.

The carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide were analyzed using a thermal conductivity detector. Similar problems in experimental design affected quantification of these analytes. In general, no nitrous oxide, carbon monoxide, or sulfur dioxide was detectable in the off-gas of the sludge surrogate (see Figure 21 [only one sample; therefore, no confidence intervals]) and Pad A nitrate salt (see Figure 22) samples, with occasional and apparently random exceptions for the sludge. Results were similar in the organic sludge waste to the organic sludge surrogate. Only carbon dioxide was routinely detectable, with most samples showing a baseline amount probably from carbon dioxide in the air used as carrier gas. Pure air injections result in similar responses. For more detailed information, see Appendix L.

Figure 23 shows a summary of the bubbler water analytical results for nitrite and nitrate in off-gas from Pad A salt ISTD and organic sludge waste composite ISTD. Bubbler volume was 100 mL (3.4 oz) initially, made slightly basic with sodium hydroxide. These measurements were made by ion chromatography using an ion chromatograph (Dionex 2000i) with carbonate/bicarbonate eluent and a sulfuric acid suppressor column. No pattern is discernable in the results, and surprisingly, organic sludge waste composite off-gas contained more measurable nitrate than did the Pad A salt. The source of this nitrate is unknown but may be related to system contamination, as previously discussed.

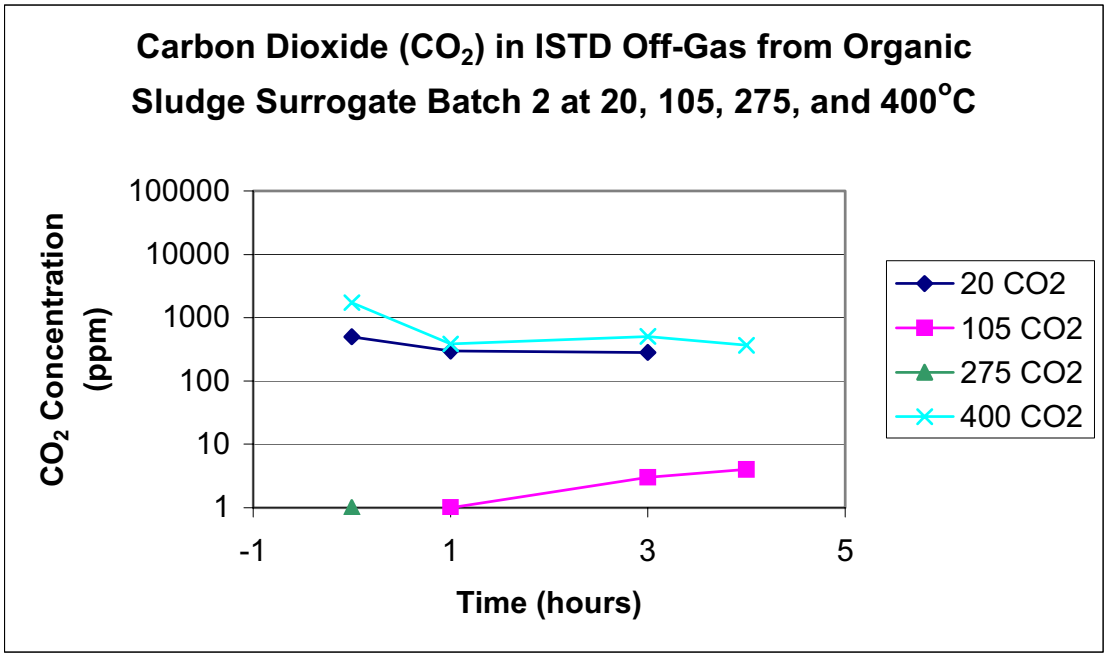

Figure 21. Carbon dioxide concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge surrogate.

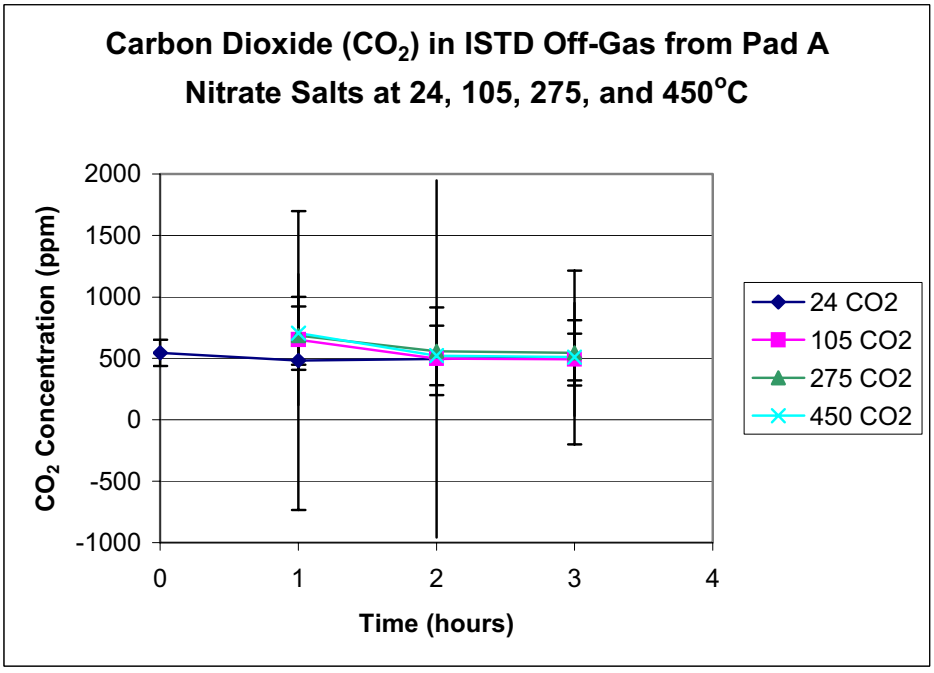

Figure 22. Carbon dioxide concentration in off-gas from ISTD as a function of time and temperature for samples of Pad A nitrate salt.

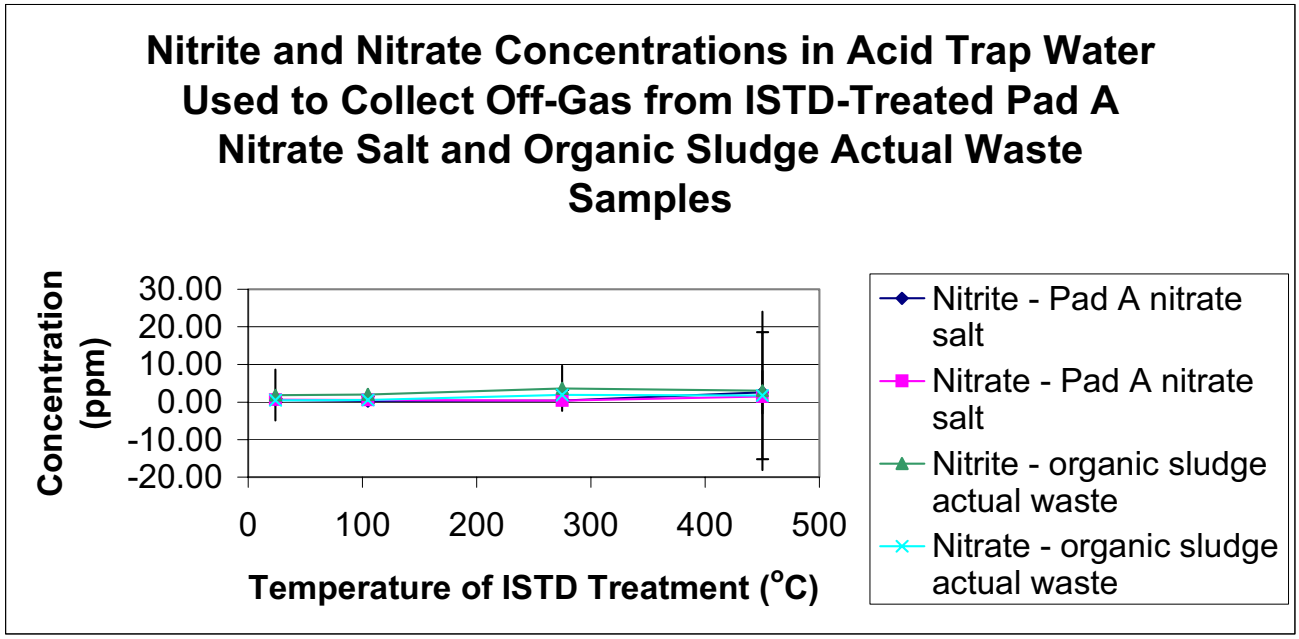

Figure 23. Nitrite and nitrate concentrations from off-gas in acid trap water for ISTD-treated samples of Pad A nitrate salts and organic sludge waste.

4.2.2.2 Filter. A 0.2-µm filter was placed in the off-gas stream to collect any radionuclide particulates released during ISTD treatment. The results were different than expected but not conclusive. The filters in the off-gas stream contained uranium during ISTD for soil (see Figure 24), inorganic sludge surrogate (see Figure 25), organic sludge surrogate (see Figure 26), organic sludge waste (see Figure 27), and Pad A nitrate salt waste (see Figure 28). For Figures 24 through 28, 95% confidence intervals are shown; some data points were below detection limits (see Table L-2 in Appendix L). The filters for organic sludge surrogate and organic sludge waste contained uranium and plutonium. Most of the measurements of filters did not detect measurable quantities (green shading on Table L-2 in Appendix L) of neptunium, americium, and plutonium. No trend in uranium was present on the filter with temperature. Also, the standard deviations and 95% confidence intervals for uranium and plutonium were generally of the same order of magnitude as the mean for uranium and plutonium, meaning that there was a lot of variability in the data and that it should be used more as qualitative rather than quantitative data.

4.2.2.3 Mass Balance. Weight loss was measured for samples treated with ISTD. The weight loss data are summarized in Figure 29 (values of individual measurements are provided in Table L-8 in Appendix L). All of the samples were heated for a 4-hour time period. As expected, the soil and Pad A nitrate salt samples showed the smallest (less than 10 wt%) change in mass on heating. These materials contain minimal amounts of organic compounds and water. The inorganic sludge surrogate samples lost about 25% of their original mass. Most of the mass loss occurred at 105°C (221°F); this is not surprising since the material contained no organics and approximately 20 wt% water. The organic sludge surrogate contained approximately 50 wt% VOCs and 29 wt% Texaco Regal Oil. Overall, the organic sludge surrogate lost more than 60% of its mass, but not until 275°C (527°F). Surprisingly, given the large percentage of volatile organics in the material, only 5% of the initial mass was lost at 105°C (221°F). Mass loss above 50% may represent loss of the more volatile elements of Texaco Regal Oil.

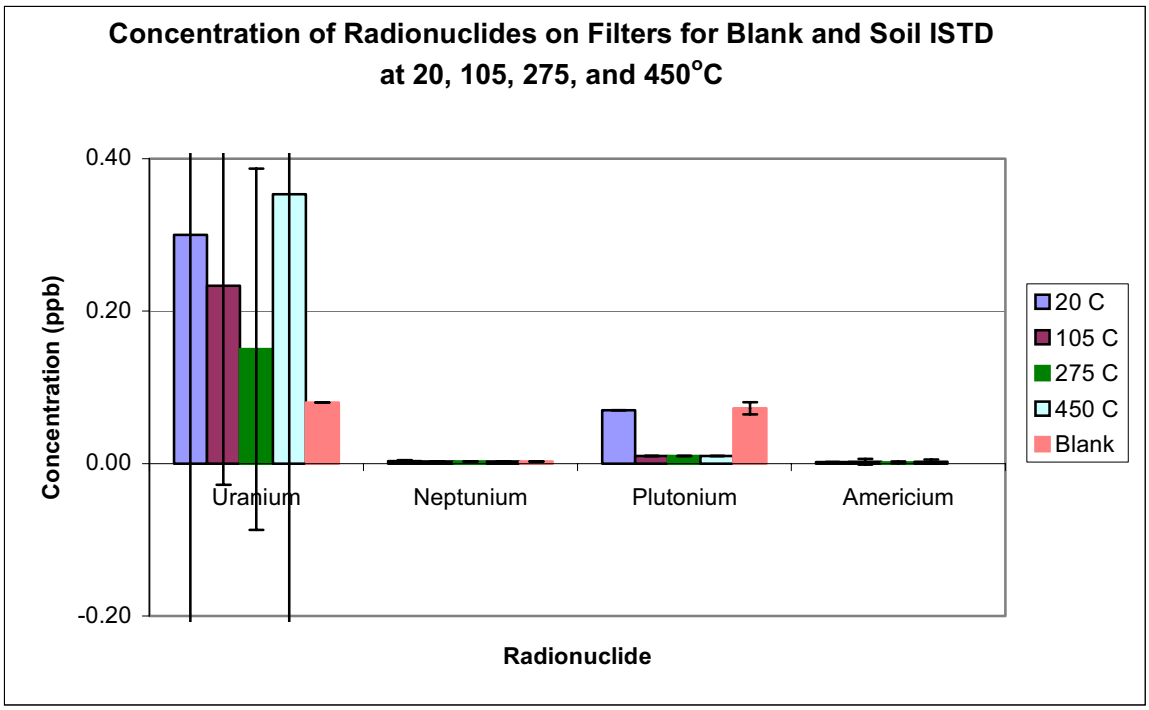

Figure 24. Concentrations of radionuclides on blank and soil ISTD filters.

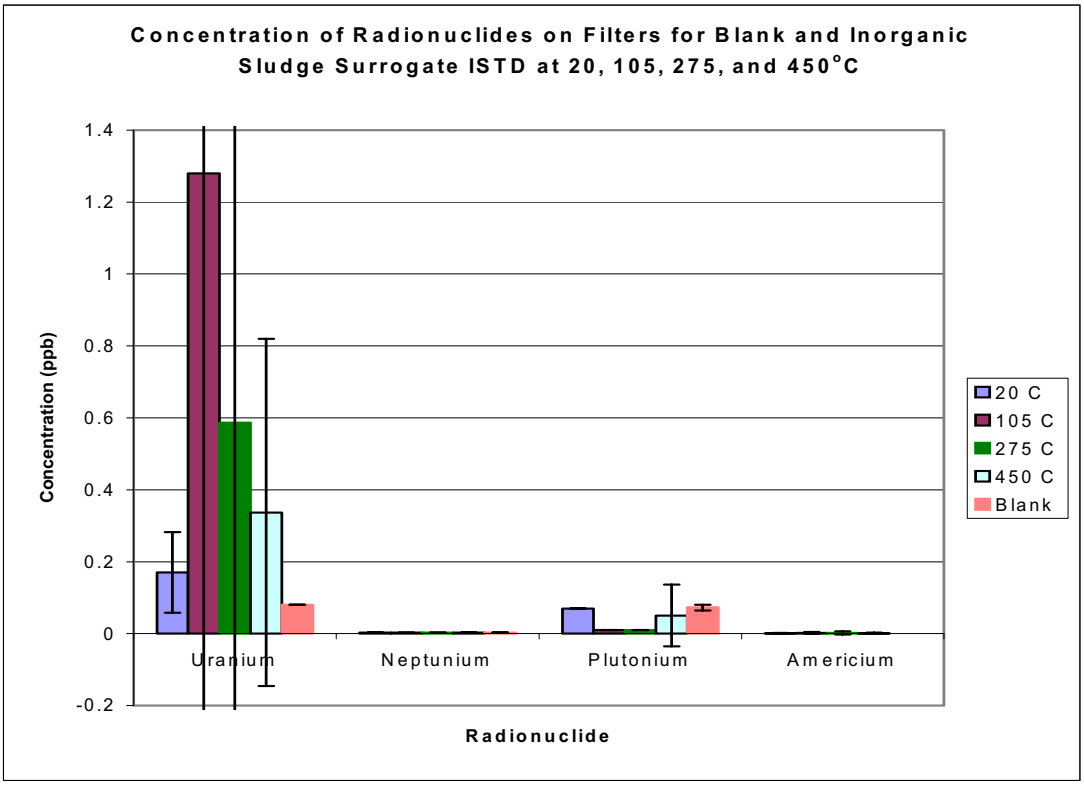

Figure 25. Concentrations of radionuclides on blank and inorganic sludge surrogate ISTD filters.

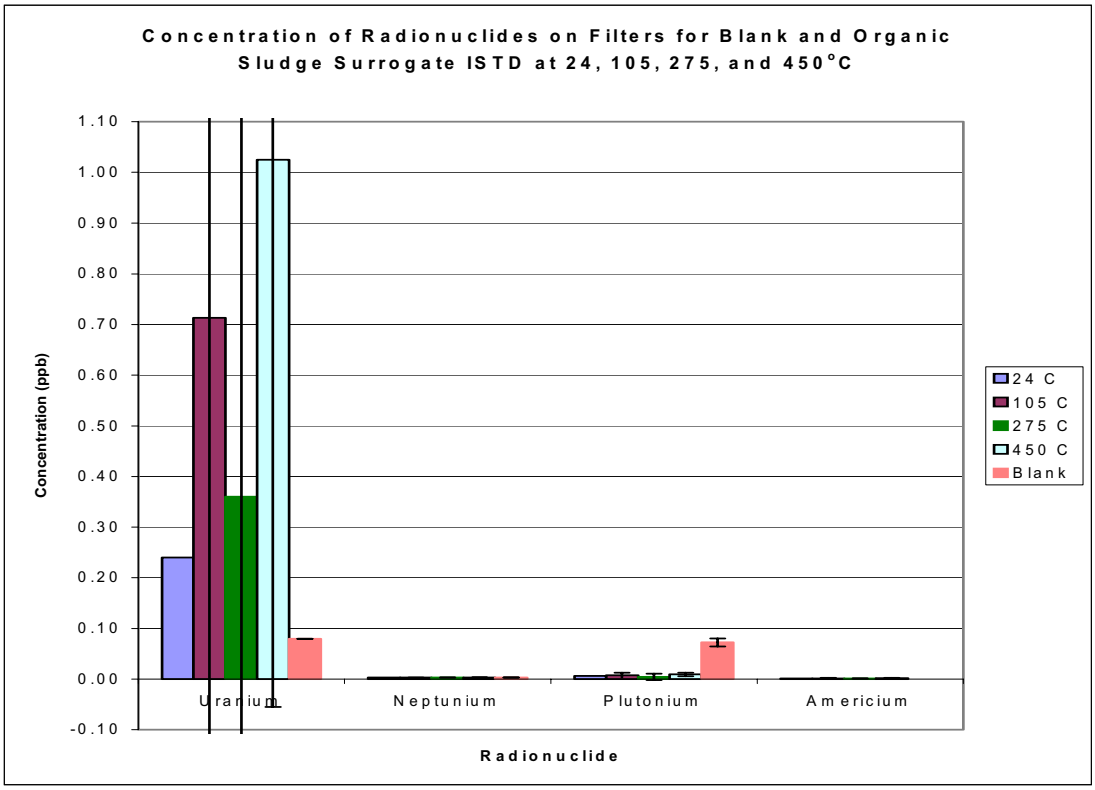

Figure 26. Concentrations of radionuclides on blank and organic sludge surrogate ISTD filters.

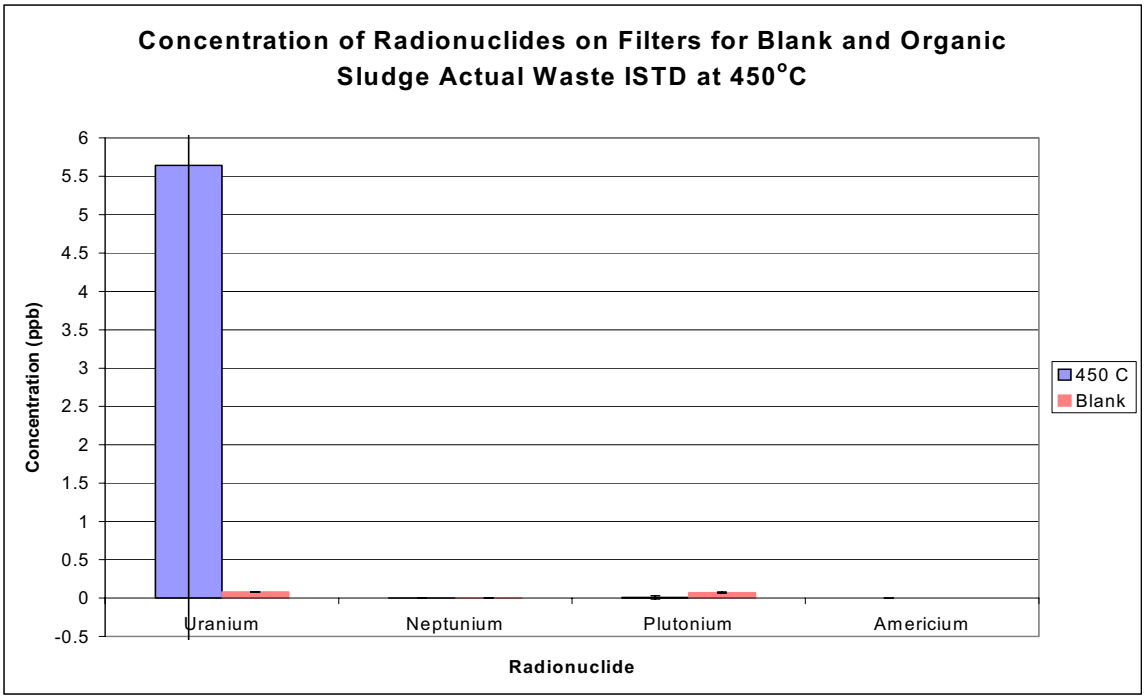

Figure 27. Concentrations of radionuclides on blank and organic sludge waste ISTD filters.

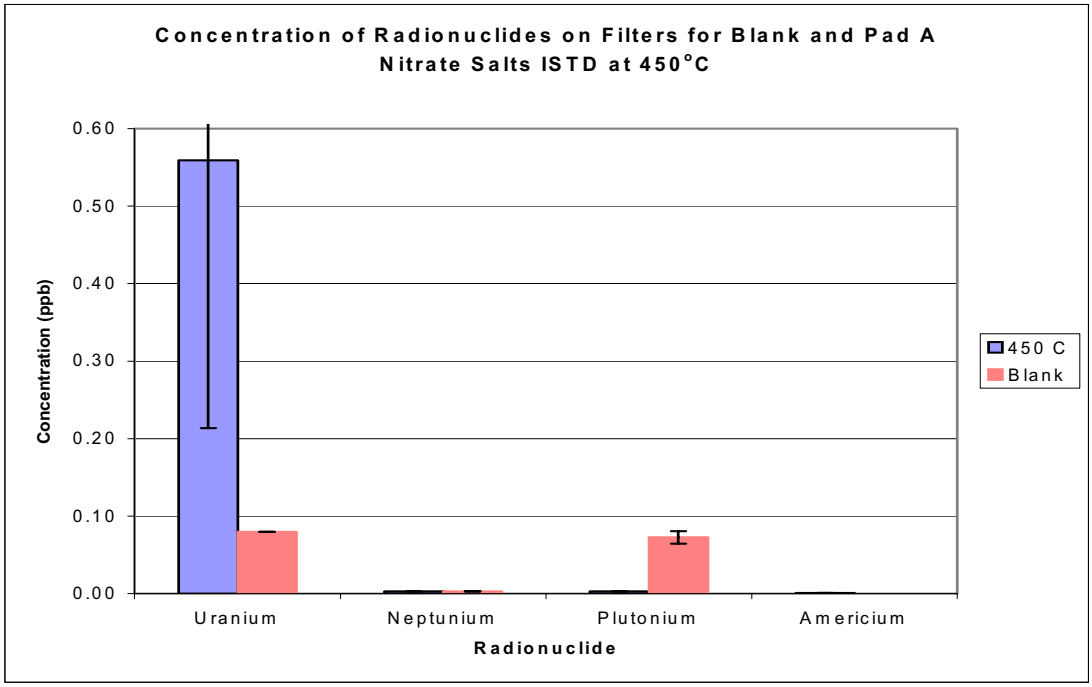

Figure 28. Concentrations of radionuclides on blank and Pad A waste ISTD filters.

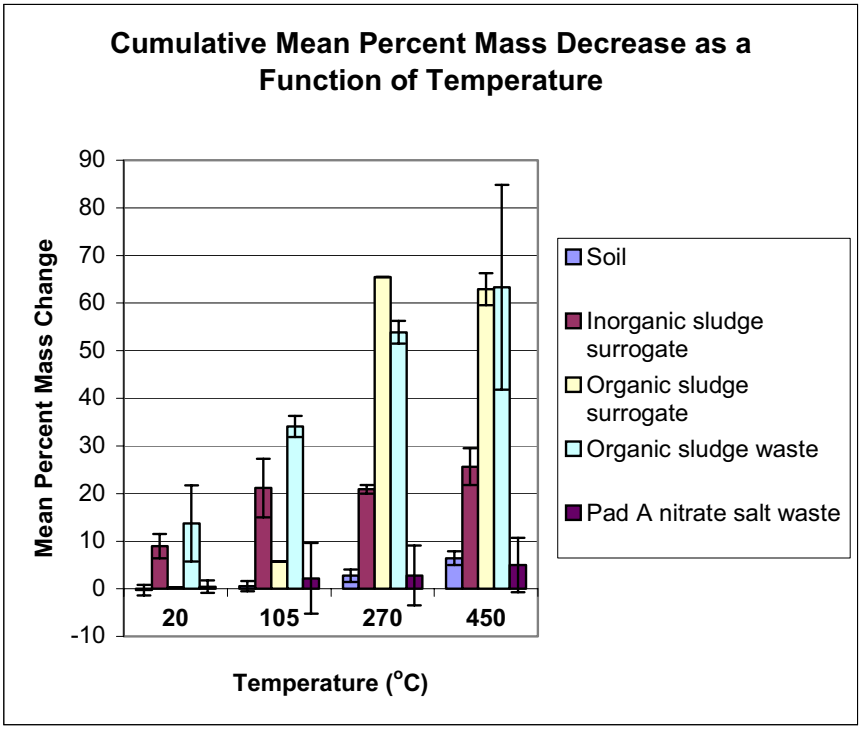

Figure 29. Cumulative mean percent mass change as a function of temperature and a duration of four hours.

Compositional analyses (radionuclide and organic compounds) for two separately prepared batches of organic sludge waste composite are shown in Table L-3 in Appendix L.

The concentration of radionuclides in each sample was measured before and after ISTD treatment. The expected concentrations of radionuclides in samples after heating were calculated based on the mean measured mass losses of samples of the material and the assumption that no radionuclides were released from the sample during heating. The results are presented in Table L-4 in Appendix L. No data were available on inorganic sludge surrogate. The data for organic sludge waste and one of the organic sludge surrogate batches suggest that americium was lost during heating, but not uranium. The data for the Pad A waste suggest that uranium and plutonium were lost during heating. Overall, the data showed considerable variation. In several cases, the measured concentration of radionuclides was greater than the expected concentration. This difference could be caused by the difference between the actual mass loss in the measured sample and the average mass loss used to calculate the expected concentration or errors in the measured concentration of radionuclides.

Table L-4 in Appendix L shows that the mean actinide concentrations increased by a factor of 1.5 to 2.5 in the posttreatment organic sludge waste composite, caused by the 50 to 60% mass loss characteristic of treated organic sludge. The possible exception was americium, which apparently decreased in concentration following heat treatment in the second trial; however, americium was not detectable on gas stream filters (see Figures 26 and 27) or in the bubbler solution. The mean concentration of uranium decreased substantially in posttreatment Pad A salt. This uranium also did not appear on the filter downstream of the heated sample or in the bubbler solution, and thus, it must be hypothesized that the uranium, americium, or both plated out on the quartz tubing immediately outside the furnace before reaching the filter. Although it was heat taped, visual amounts of organic material also plated there.

In conclusion, the filter and composition data are not consistent with respect to release of radionuclides during ISTD. Uranium and plutonium are seen on the filters for several waste materials, while americium apparently decreased in organic sludge surrogate and waste samples during heating. In all cases, the 95% confidence intervals are the same order of magnitude or larger than the mean values. Given the inconsistent picture presented by the data, conclusions about the fate of radionuclides during ISTD treatment cannot be made. Additional testing and controls (including a detailed full mass balance) would be necessary to confirm the extent of potential radionuclide release during ISTD.

4.3 Determine the Degree of Hazardous Organic Contaminant and Nitrate Removal or Destruction from Soil and Waste

In situ thermal desorption can remove organic compounds from the waste. Lower temperatures (100 to 200°C [212 to 392°F]) are appropriate for removing VOCs and water; this is the temperature range of interest for the SDA. Higher treatment-zone temperatures (above 200°C [392°F]) are used for removing and destroying semivolatile compounds. Treatment-zone temperatures of 400 to 500°C (752 to 932°F) have been used to remove and destroy polychlorinated biphenyls at some field sites (TerraTherm 2005b; TerraTherm 2005c; U.S. Navy 1997). The removal will be a combination of vaporization and thermal destruction, depending on the temperature, materials, and oxygen present. Section 4.3.1 covers work completed by MSE on nonradioactive surrogates. The MSE tests were larger drum-scale tests. Section 4.3.2 covers ISTD of radioactive surrogate and waste completed at the INL Site, and was performed on a smaller scale using surrogate and waste that was ISTD treated. The second set of tests was used to confirm that the MSE drum-scale tests matched what would occur using the radioactive waste and surrogate.

4.3.1 MSE Drum Test

Tests at MSE were conducted with nonradioactive surrogates for organic sludge and nitrate salt. Plots of the temperature of drum contents and volatile and acid gas emissions during heating are presented in Section 4.2.1 of this report. Analyses of drum residues post-ISTD are presented in this section.

For the organic sludge surrogate test, analysis of posttest drum solids showed residual concentrations up to 0.2 wt% of the four feed VOCs, indicating that the VOCs had been mostly, but not completely, volatilized. For the nitrate salt surrogate test, posttest examination of the drum contents and heater assembly showed that the nitrate salt feed material had foamed, nearly plugging the test drum off-gas outlet and clearly indicating some degree of thermal decomposition of the drum contents. Laboratory analysis of pretest and posttest drum solids indicated that the nitrate concentration of the feed was essentially unchanged by processing, suggesting relatively minor decomposition or other removal of the nitrate salts. For the mixture of organic sludge surrogate and combustibles, analysis of posttest drum contents showed low concentrations of residual halogenated organic feed constituents, less than 150 mg/kg in all instances.

4.3.2 ISTD with Radioactive Surrogates and Waste

Laboratory-scale ISTD tests were conducted with radioactive surrogates and waste.

The mean change in mass for soil, inorganic sludge surrogate, organic sludge surrogate, Pad A nitrate waste, and organic sludge waste treated with ISTD at various temperatures is presented in Figure 29. As expected, the mass of the soil remained fairly constant with a mass loss of less than 10%, even at a temperature of 450°C (842°F). Pad A nitrate salt behaved in a similar manner with a mass loss of less than 10% for all temperatures. The inorganic sludge surrogate showed a mass loss of approximately 20%, which occurred at 105°C (221°F) and did not increase as the temperature increased to 450°C (842°F). This mass loss is most likely caused by removal of water from the surrogate. The organic sludge waste showed a greater percent mass loss than the organic sludge surrogate at 105°C (221°F). The reason for this is not clear; it is possible that the waste may have contained more water than the surrogate. The percent mass loss at 275 and 450°C (527 and 842°F) was the same for the organic sludge surrogate and waste.

The primary benefit expected from the ISTD process at the SDA is for organic destruction or removal. Removal or destruction of organics provides the obvious benefit of contaminant removal, but as a pretreatment to grouting, it also creates a more easily grouted waste form. The presence of high concentrations of organics greatly impacts the ability of grout to form stable monoliths. The results of ISTD organics removal showed that the ISTD process does, in fact, provide a benefit by removal of significant amounts of organics and creation of a waste form that can be more successfully grouted; however, based on reactivity results from Section 4.4, the potential for uncontrolled exothermic reactions is too high, and the ISTD process is not recommended for the types of waste and debris encountered at the SDA.

4.4 Test Potential Mixtures of Organics and Nitrates for Reactivity

All drum tests and thermal gravimetric analysis (TGA) tests in this section were performed with nonradioactive surrogates. Differential scanning calorimetry (DSC) tests were done with nonradioactive surrogates or waste, as noted.

4.4.1 Thermal Gravimetric and Differential Scanning Calorimetry Testing

Thermal gravimetric analysis was performed on individual surrogates and mixtures of surrogates. Previously collected DSC data on waste also are included for completeness.

Instrumental thermal analyses (such as DSC and TGA) are analytical techniques that characterize specific heat, enthalpies of transition, reactivity, temperature of reaction, and magnitude of reaction during heating. Instrumental thermal analyses are small-scale measurements (0.02 to 0.1 g [0.0007 to 0.004 oz]) using a bench-top laboratory instrument. The result is a graphical output of exotherms (heat given off, positive heat flows on graphs) and endotherms (heat absorbed, negative heat flows on graphs) (i.e., heat given off or heat absorbed versus system temperature).

The DSC provides good thermal resolution but lacks the ability to obtain weight data as heating progresses. The TGA is similar in calorimetry operation to DSC but, in addition, provides weight loss data while heating takes place.

In addition to nitrate salt surrogate and organic sludge surrogate (see Tables A-2 and A-3, respectively, in Appendix A), three surrogates containing carbon (graphite, carbon powder, and paraffin) were chosen that could be mixed on a very small scale and simulate prevalent waste types containing carbon that might be encountered in RFP waste.

Organic sludge surrogate was used alone and also has been reactivity tested before, both by DSC and macrotesting (Dick 2001). The three surrogates containing carbon provide a range of reactivity potential with nitrate salts covering the probable organic waste that could be in proximity with nitrate salts.

The TGA tests were run to 900ºC (1,652ºF) at a heating rate of 10ºC (18ºF)/minute, 1ºC (1.8ºF)/minute, 0.5ºC (0.9ºF)/minute, and 0.1ºC (0.18ºF)/minute. All are heat rates faster than the typical field rate of 0.01 to 0.005ºC (0.018 to 0.009ºF)/minute because of the limits of the instrument. Replicates were run on the single surrogates and several mixtures of surrogates.

Results of the TGA run on nitrate salt surrogate are depicted in Figure 30. The DSC of the RFP nitrate salt waste tested at Brookhaven National Laboratory gave similar results (Milian et al. 1997). Minor differences appear between the two; this is expected since the nitrate salt waste and the nitrate salt surrogate are similar but not identical in composition.

Three major endothermic features are noted. Below 100ºC (212ºF), the DSC has two peaks and the TGA one peak that correspond to the loss of water hydration. Following this, both plots show the transition peak for potassium nitrate (131ºC [267.8ºF]) and the composite eutectic melting point (210 to 240ºC [410 to 464ºF]) for sodium and potassium nitrates. For both salt samples, a minor peak is seen in the thermo analysis around 380 to 420°C (716 to 788ºF), which is apparently a reaction of salt with the 1 wt% organic (see Table A-2 of Appendix A) expected to be present in the nitrate salt waste and added in the form of EDTA to the nitrate salt surrogate.

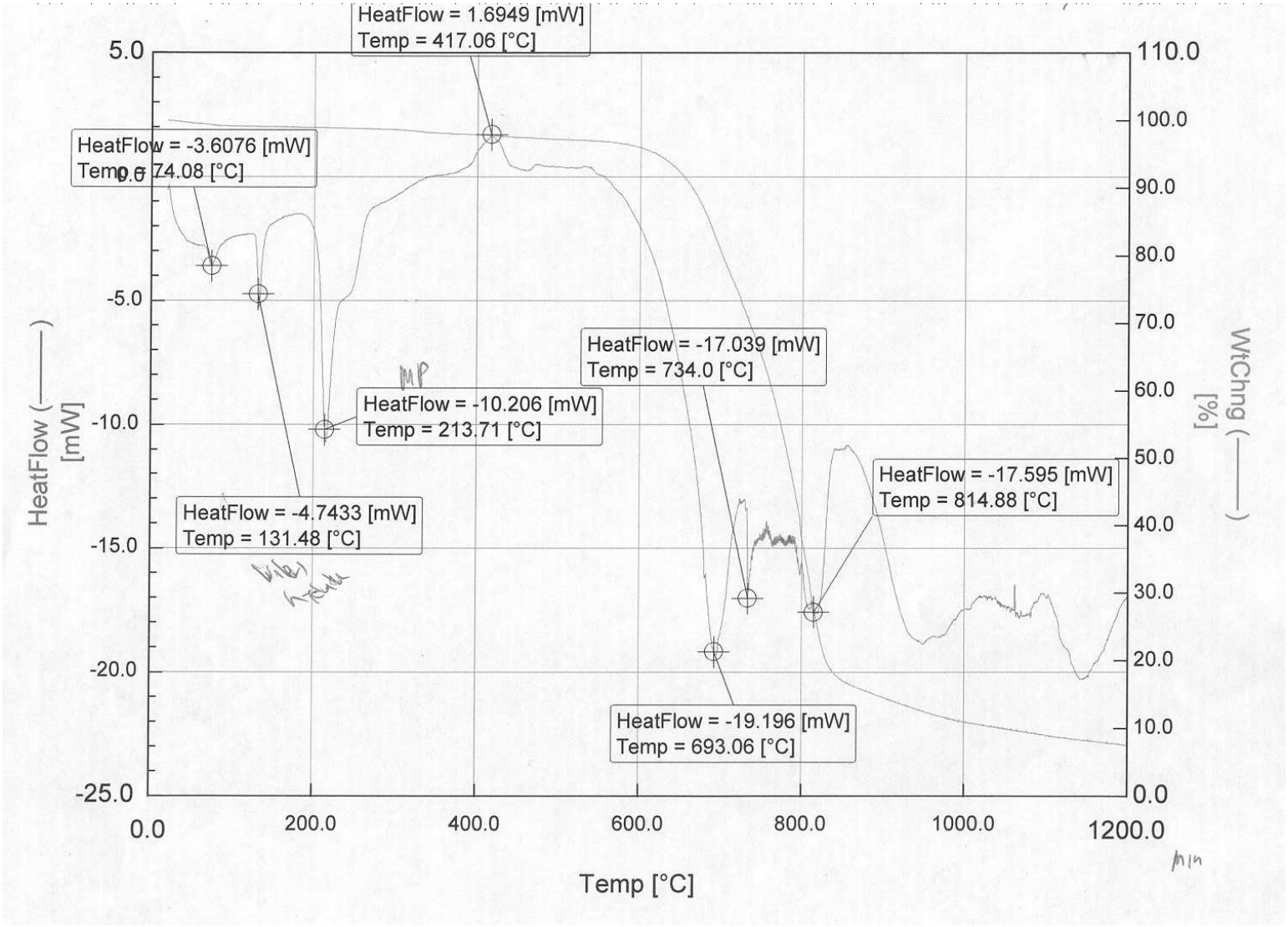

Figure 30. Thermal gravimetric analyses of nitrate salt surrogate run at 10°C (18°F)/minute.

The nitrate salt surrogate sample was heated to higher temperatures than the nitrate salt waste sample; the waste would be expected to behave similarly to the surrogate. Heating salt surrogate alone well past the eutectic melting point of 210 to 240°C (410 to 464ºF) and beyond the reported decomposition temperature (380°C [716ºF]) is required to eventually decompose nitrates (CRC 2000). According to the TGA weight curve, this occurs at 500 to 650°C (932 to 1,202ºF).

The results of thermal analysis for the organic sludge surrogate alone show a broad combustion range in Figure 31. The organic sludge surrogate was run at 1ºC (1.8ºF)/minute. An exothermic reaction, probably combustion of the oil (heat released and mass decreased), was present to about 400°C (752ºF), at which point the heat release slope increased, suggesting the reaction mechanism changed. As evidenced by the multiple slopes and peaks, several reaction mechanisms were present during the heating process, and all resulted in a decrease of mass. The sludge is not a pure component, so the multiple peaks could indicate the reaction, the combustion, or both of different portions of the sludge.

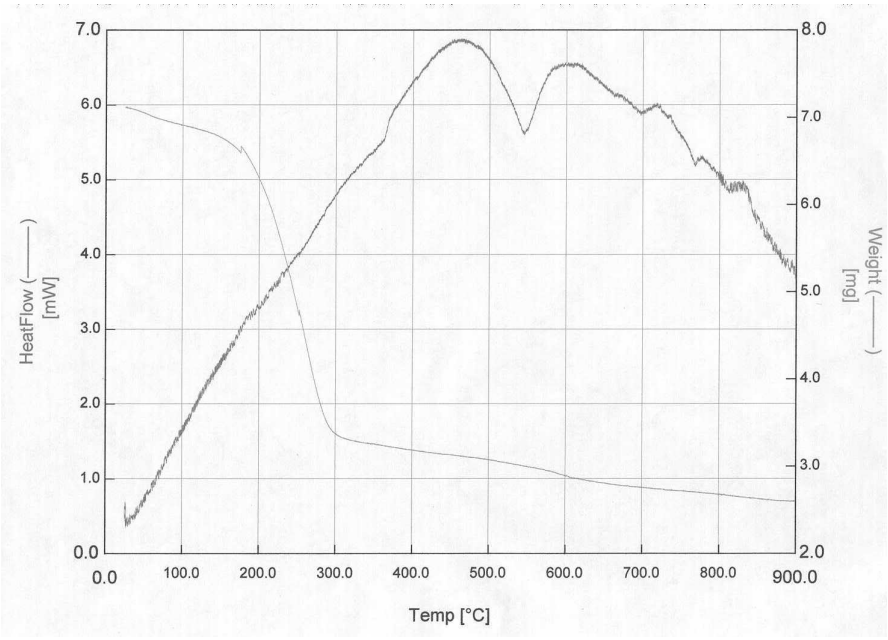

Figure 31. Thermal gravimetric analyses of organic sludge surrogate run at 1°C (1.8°F)/minute.

Thermo analysis was run on four mixtures of carbon (carbon powder, graphite, paraffin, and organic sludge surrogate) and nitrate salt surrogate. With regard to nitrate salt surrogate, the carbon powder was the most reactive form of carbon tested. The carbon powder simulates charred debris; the paraffin simulates plastics in debris, and the organic sludge is a common organic source in the waste.

Results of the nitrate salt surrogate and carbon powder mixture are discussed first. The salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the endotherm [actual or relative] in that temperature range in Figures 32, 33, and 34). The rate of temperature increase in TGA testing affects the temperature of onset, the magnitude, and the duration of the major exothermic reaction. At a heating rate of 10°C (18°F)/minute (see Figure 32), the system remained endothermic until around 275°C (527°F); the major exothermic reaction started around 375°C (707°F) and was completed around 430°C (806°F), with a mass loss of 62%, and a very sharp peak, having a maximum heat flow of 245 mW, was observed. A second, much smaller, exothermic peak was observed between 430 and 460°C (806 and 860°F) (with a mass loss of 3%). The percent mass loss rate during the major exothermic reaction was approximately 11%/minute.

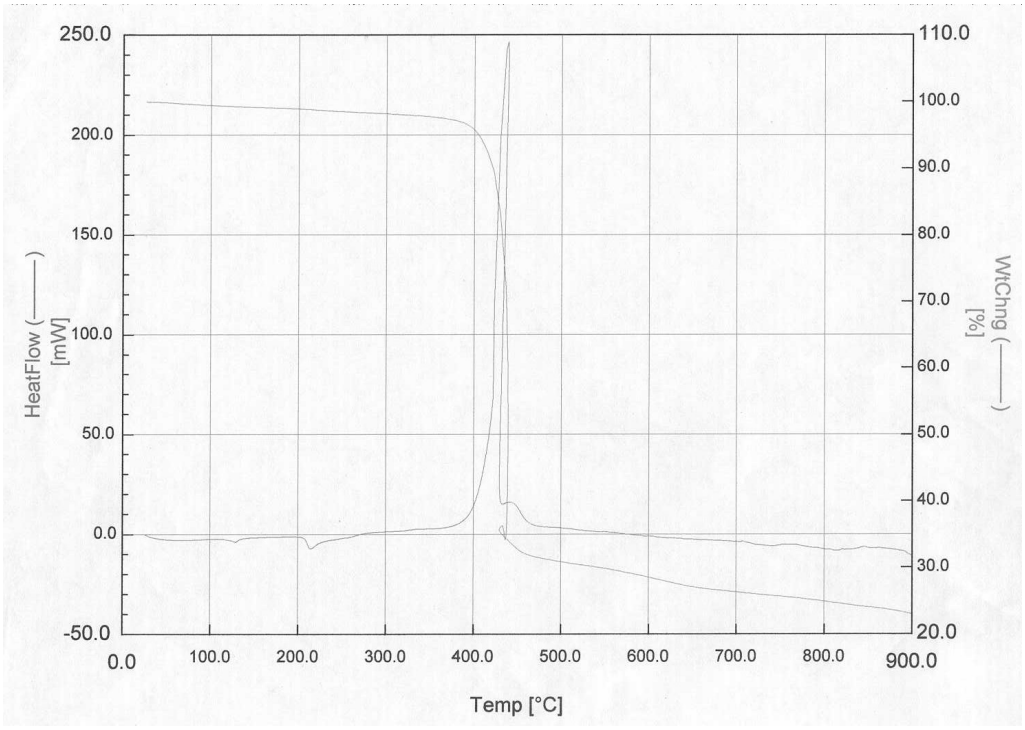

Figure 32. Thermal gravimetric analysis of a mixture of 83 wt% nitrate salt surrogate and 17 wt% carbon powder at 10°C (18°F)/minute.

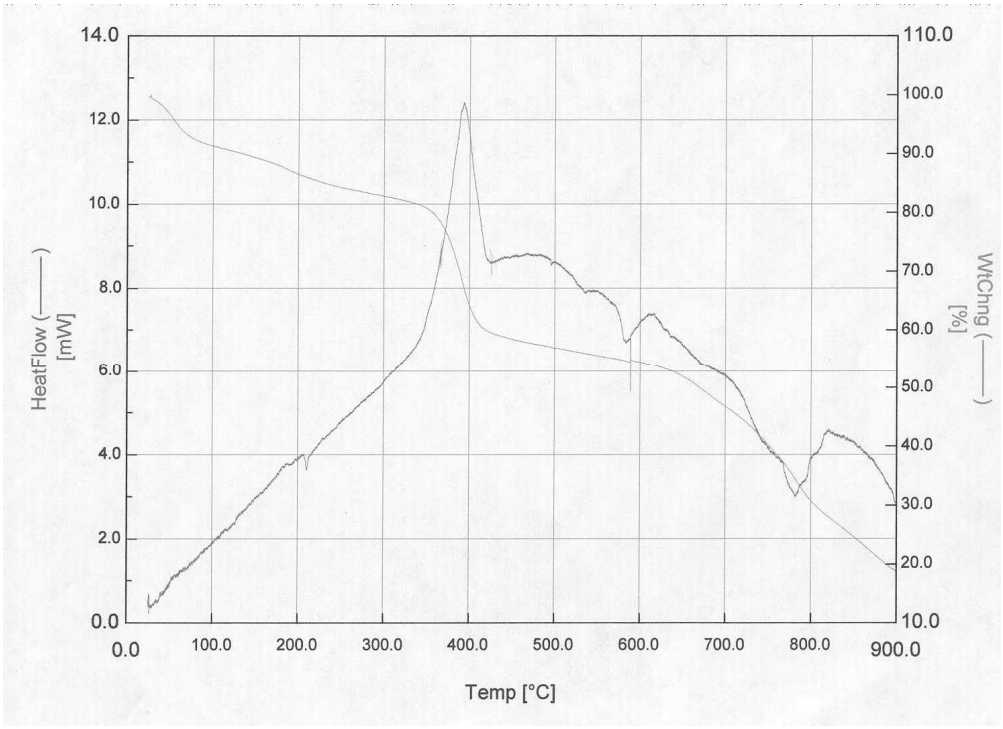

Figure 33. Thermal gravimetric analysis of a mixture containing excess carbon with respect to nitrate salt surrogate run at 1°C (1.8°F)/minute.

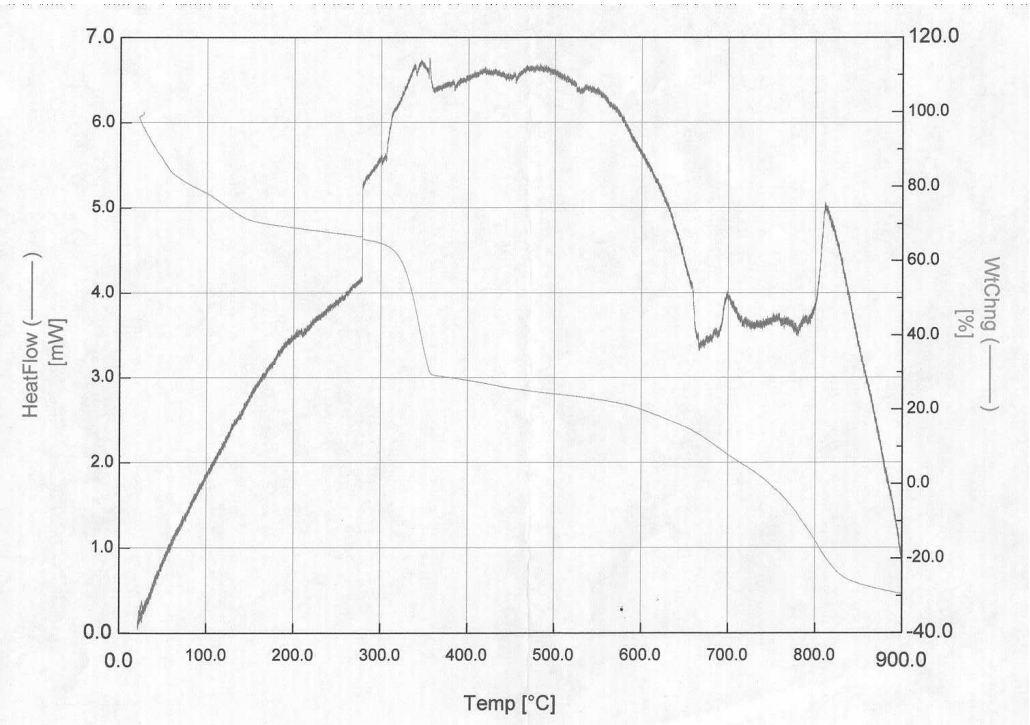

Figure 34. Thermal gravimetric analysis of a mixture of 83 wt% nitrate salt surrogate and 17 wt% carbon powder at 0.1°C (0.18°F)/minute.

At a heating rate of 1°C (1.8°F)/minute (see Figure 33), the system was exothermic from the start; the major exotherm (note the inflection in the heat release trace) started at approximately 350°C (662°F) and finished at approximately 425°C (797°F), with a 22% mass loss; a well-defined peak with a maximum heat flow of 12.4 mW was observed. The second exothermic peak was observed at 425 to 590°C (797 to 1,094°F), with a mass loss of 5%, and was more substantial than the second peak observed at the faster heating rate. The percent mass loss rate during the major exothermic reaction was approximately 0.29%/minute.

At a heating rate of 0.1°C (0.18°F)/minute (see Figure 34), the system was exothermic from the start; the major exotherm (note the inflection in the heat release trace) started at approximately 275°C (527°F) and finished at approximately 360°C (680°F), with a 37% mass loss; a peak with a maximum heat flow of 6.8 mW was observed. The second exothermic peak was observed at 425 to 590°C (797 to 1,094°F). This peak had a maximum heat flow of 6.6 and was much broader than at higher heating rates; a mass loss of 15% was observed. The percent mass loss rate during the major exothermic reaction was approximately 0.044%/minute.

A DSC run (see Figure H-10 in Appendix H [ITRP 1999]) of a stoichiometric mixture of nitrate salt waste and graphite (87-13 mass ratio) looks quite different from the TGA run performed with a near stoichiometric mixture of nitrate salt surrogate and carbon powder (83-17 mass ratio) shown in Figure 32. The nitrate salt waste and graphite mixture exhibits all endotherms, except for a small (<4.4 mW = <0.2 mW/mg × 21.81 mg) relative exothermic peak around 400°C (752°F). The exothermic reaction occurs at the same temperature for both mixtures, but the magnitude of the reactions is much greater for the mixture containing carbon powder than for the mixture containing graphite. While graphite and carbon powder have the same elemental composition, C, the structure of the two forms of carbon is very different. Graphite has a definite crystal structure, while carbon powder is amorphous. The carbon in

graphite is much less available for reaction than the carbon in carbon powder; this could be the reason that the reaction with carbon powder was much more exothermic than the reaction with graphite.

The reaction of nitrate salt surrogate with paraffin also was evaluated. As with the nitrate salt surrogate and carbon powder, the salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the endotherm) in that temperature range in Figure 35. The rate of temperature increase in TGA testing affects the temperature of onset, the magnitude, and the duration of the major exothermic reaction. At a heating rate of 10°C (18°F)/minute (see Figure 35), the system remained endothermic until around 330°C (626°F), and the major exothermic reaction started around 330°C (626°F) and was completed around 520°C (968°F); a sharp peak with a maximum heat flow of 24 mW at 480°C (896°F) was observed. A second, much smaller, exothermic peak was observed between 520 and 630°C (968 and 1,166°F) (with a mass loss of 3%). Approximately 28% of the initial sample mass was lost during the major exothermic reaction, while 7% of the initial mass was lost before the major exothermic reaction, and 43% was lost after. The percent mass loss rate during the major exothermic reaction was approximately 1.5%/minute.

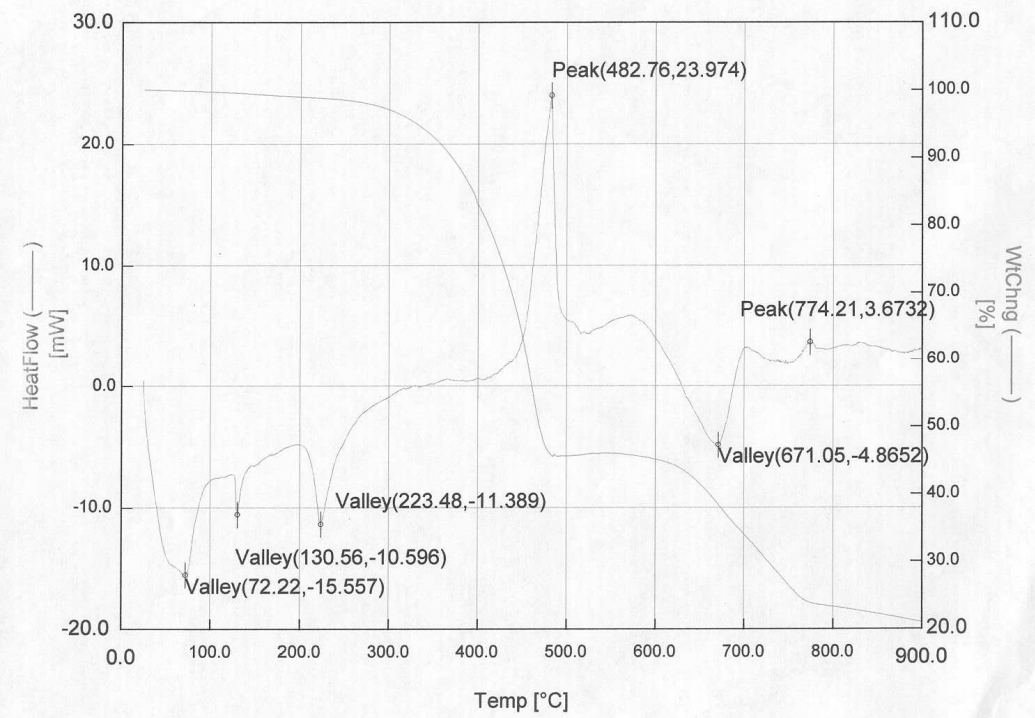

Figure 35. Thermal gravimetric analysis of a mixture of nitrate salt surrogate and paraffin at 10°C (18°F)/minute.

A second test was run with a temperature increase of 0.1°C (0.18°F)/minute. No endothermic region was observed before the major exotherm. The major exotherm during this run was very broad and peaked at 330°C (626°F) with a maximum heat flow of 5 mW. Mass data were not available for this run.

The reaction of nitrate salt surrogate with organic sludge surrogate was evaluated at a temperature increase rate of 1°C (1.8°F)/minute (see Figure 36). The plot does not exhibit an endotherm before the major exotherm. As with the nitrate salt and carbon powder, the salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the relative endotherm) in that temperature range in Figure 36. The major exotherm is very broad and peaks at about 380°C (716°F) with a maximum heat flow of

4.5 mW. The mass loss curve shows regions of decreased slope (slower mass loss); these regions coincide with relative endotherms. Some of the relative endotherms may be caused by vaporization of lower boiling compounds with the organic sludge surrogate. A secondary exotherm is also present and forms a broad peak. This plot is similar to organic sludge alone in Figure 31 and previous Brookhaven National Laboratory DSC scans of nitrate salts and oil in the sludge. The organic sludge nitrate thermo analysis shows a broad combustion area over several hours of heating. This type of combustion could be beneficial, supplementing the heat of the electrical heaters and reducing the load on the off-gas system.

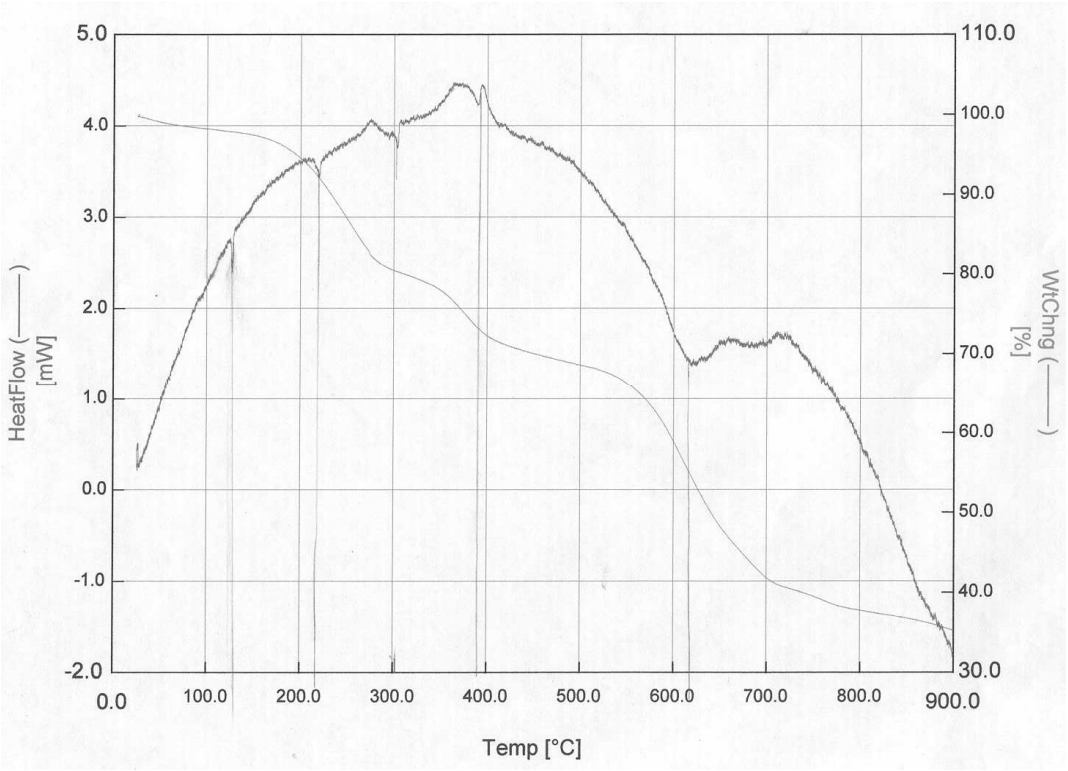

Figure 36. Thermal gravimetric analysis of a mixture of nitrate salt surrogate (56 wt%) and organic sludge surrogate (44 wt%) at 1°C (1.8°F)/minute.

4.4.2 Testing at the Energetics Materials Research and Testing Center

The purpose of this test series was to evaluate the potential of heating potentially reactive mixtures of nitrate salts, organic compounds, and carbon (the three major RFP waste types of concern) in a controlled manner similar to the conditions expected to exist during ISTD. The object was to remove or destroy most organic compounds and nitrate salts within the waste.

Three carbon-containing surrogates were tested: graphite powder, organic sludge, and combustible debris. Four heating campaigns were conducted, two being run on the first mixture of graphite powder and nitrate salts. All tests in Section 4.4.2 were conducted with nonradioactive surrogates.

4.4.2.1 Test 1—Nitrate Salt Surrogate and Graphite. This test was performed on a full drum of graphite powder intimately mixed with nitrate salt surrogate. The first heating (Phase 1) was performed with a slow cycling of the central heater and additional heat added on the outside from low-wattage, home, roof-gutter heaters around the drum, which was not insulated. The temperature profile for Phase 1 of the test is found in Figure 37. The heater made large high-to-low swings during heatup; a space

between the inside wall of the well casing and the heating tube causes the temperature of the drum contents to be lower than the heater and lag (in time). The temperature inside the drum cooled a little during the last part of the test. This cooling effect was attributed to a winter storm and cold weather that reduced the ambient temperature about 20 to 30ºC (68 to 86ºF). The weather proved to be cold enough that a maximum center temperature of only 250ºC (482ºF) and drum wall temperature of 125ºC (257ºF) were achieved over a period of 15 days.

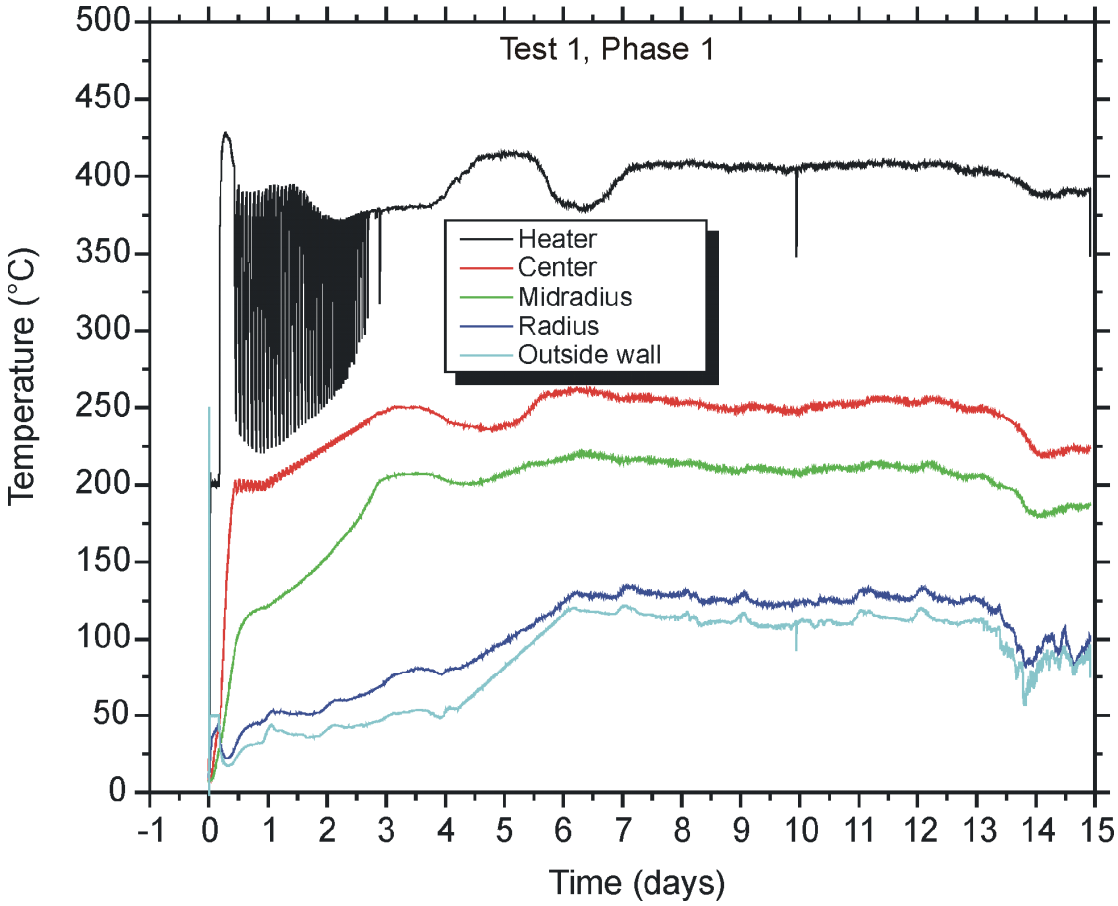

Figure 37. Temperatures within drum during Phase 1 of Test 1: nitrate salt surrogate and graphite.

The test drum was allowed to cool. Insulation was added around the gutter heaters for the second heating campaign. Phase 2 of Test 1 also lasted for about 15 days (see Figure 38). The entire mixture achieved a higher temperature with the insulation and the drum wall, and center temperatures were closer. As the temperature of the system rose, the heater was programmed for an increasing rate of heating, thus cycling at a faster rate. During the final stages of the test, the heater was removed from the controller and remained on continuously. The temperature profiles were uneventful until the last day (see Figure 38). Weight loss accelerated with the increase of temperature. Phase 2 of the test was terminated on the 15th day when a reaction reached a temperature and pressure high enough to bulge the lid, which caused seal failure on the right-hand side of the drum. This failure was followed by ejection of molten contents, which covered an area of soil and rocks for approximately 7.6 m (25 ft) outward. When hardened, the area had a silvery, shiny texture. A reaction occurred at a center temperature slightly above 425ºC (797ºF), reaching 535ºC (995ºF) and a radius temperature of 445ºC (833ºF) before instrumentation was lost. The drum lost a total of 22.2 kg (49 lb) of sample material.

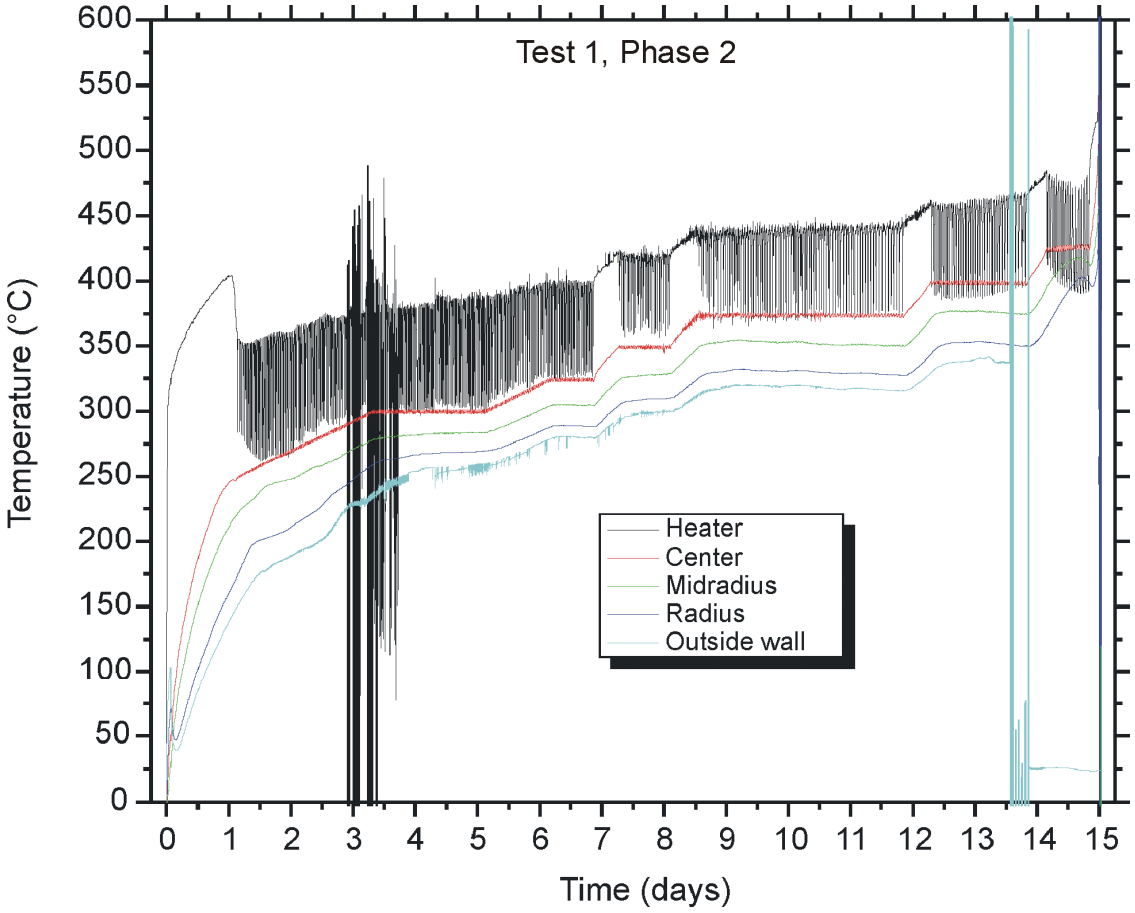

Figure 38. Temperature of drum contents at several locations as a function of time for Phase 2 of Test 1.

4.4.2.2 Test 2—Nitrate Salt Surrogate and Organic Sludge Surrogate. Test 2 was performed on a mixture of nitrate salt surrogate and organic sludge surrogate. Controlled heating by cycling the heater on and off again was used. The test was the shortest of the series, lasting about 3 days. The drum was heated at a mean rate of 0.3ºC (0.54ºF)/minute. A temperature profile of the results can be seen in Figure 39. The reading started fluctuating wildly at 70 hours into the test. The chlorinated solvents evaporated rapidly, while the oil both reacted with air and nitrate salts and evaporated. Eventually, some amount of the oil collected in the insulation and subsequently ignited and burned. The burn destroyed the thermocouple wires, causing extensive noise in the test data output. The data collected are quite difficult to interpret, but the best estimate is that the burning or nitrate reaction occurred around 250ºC (482ºF). The reaction probably started at approximately 46 hours into the test. Both the midradius and the radius thermocouples recorded an accelerating temperature rise, with the midradius temperature peaking at 478ºC (892.4ºF). The radius temperature leveled off at approximately 212ºC (413.6ºF). During this period of accelerating temperatures, the heater shut off at 54 hours and did not turn on until 16 hours later. Almost all the organic sludge surrogate apparently reacted or evaporated, leaving a residue of a 25-cm (10-in.)-thick, drum-diameter-size, gray and white material.

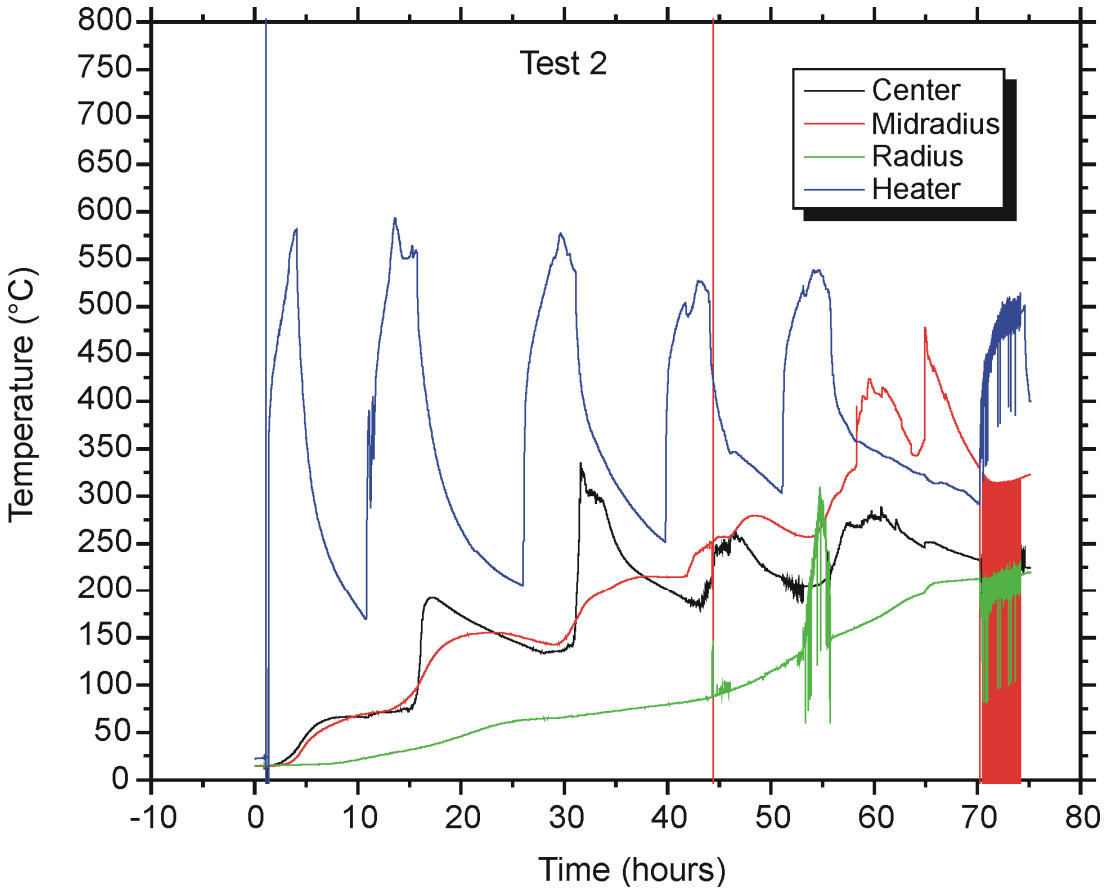

Figure 39. Temperature of drum contents at several positions as a function of time during Test 2.

4.4.2.3 Test 3—Nitrate Salt Surrogate and Combustible Debris. Test 3 used a mixture of combustible debris and nitrate salt surrogate. The heater was set to cycle not more than 100ºC (212ºF) above the center test mixture. The starting temperature of the system was 36ºC (96.8ºF). The sample material ignited at 131 hours (approximately 5 days). At the temperature of reaction, the midradius was 109ºC (228.2ºF), and the radius was 81ºC (177.8ºC). The ignition temperature recorded by the computer logger was 220ºC (428 ºF) at the center thermocouple (see Figures 40 and 41).

The period from the point of reaction until the lid blew off was 72 seconds. Peak temperatures from the profiles should be taken with some reservations, since the data were only recorded every 2 seconds. Note from the temperature profiles that the time interval between the reaction at the center and the reaction at the radius was 22 seconds. The burning material (deflagration) produced pressure high enough and fast enough to dome the lid before pushing the lid and locking ring upward from the drum. The lid and heating apparatus were found next to the drum in the horizontal position. The heater was undamaged except for some melted insulation on the leads. A considerable number of absorbent wipes were found downwind of the test, which would indicate that the sample material in the upper part of the drum did not burn before the pressure built up in the drum. Ash from the cotton rags was scattered over a 22.9-m (75-ft) radius of the surrounding area.

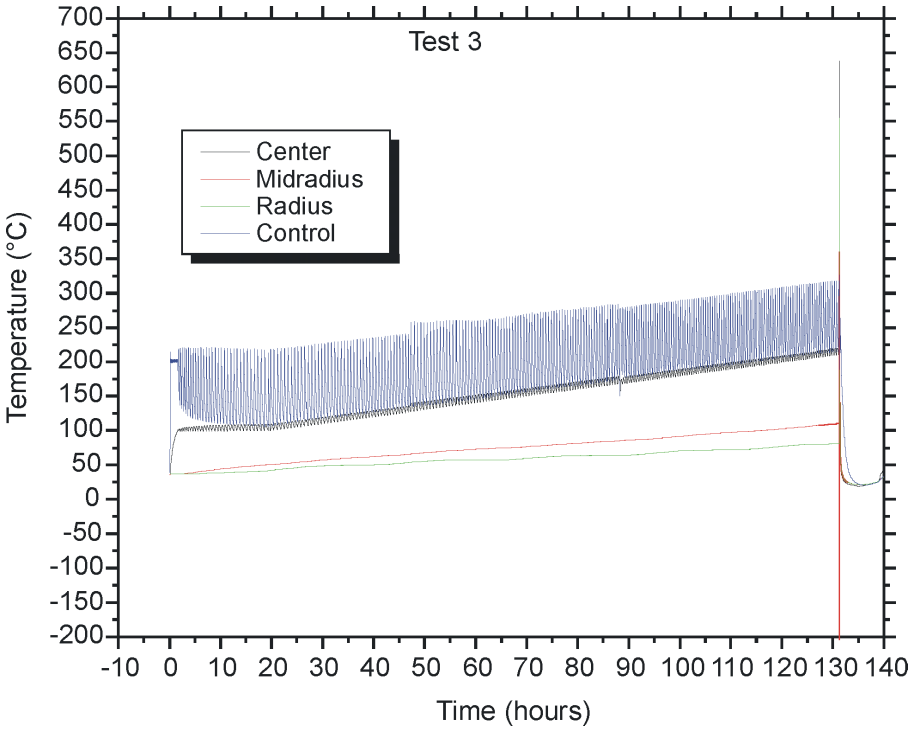

Figure 40. Temperature versus time for drum contents at three positions for drum Test 3—nitrate salt with debris.

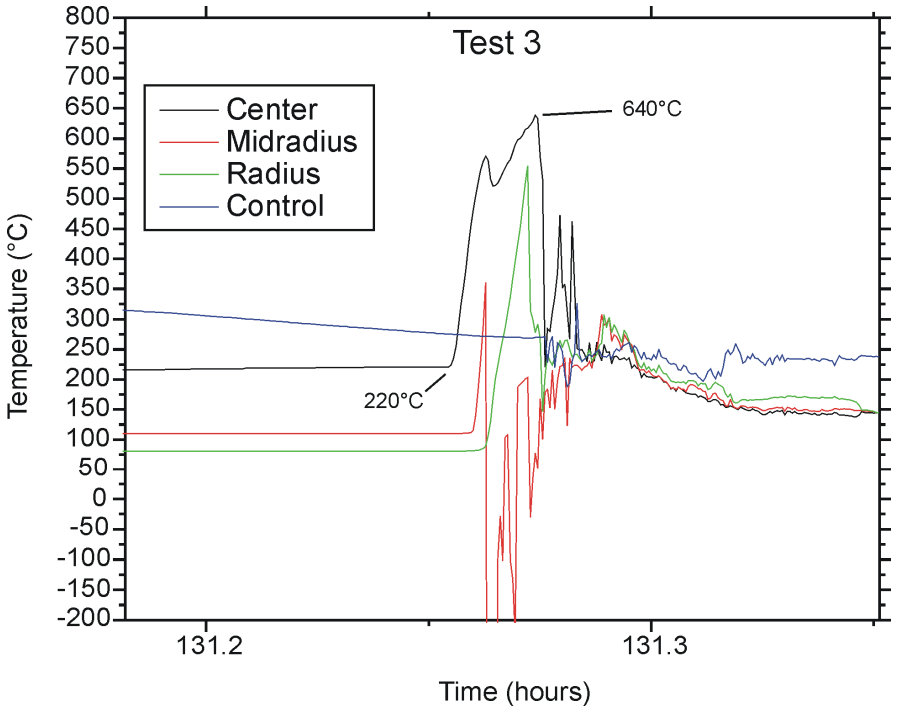

Figure 41. Expansion of time period of greatest reactivity for temperature versus time for drum contents at three positions for drum Test 3—nitrate salt with debris.

4.4.3 Reactivity Summary

For mixtures of nitrate salt surrogate and carbon, the rate of temperature increase in the TGA testing affects the temperature of onset, the magnitude, and the duration of the major exothermic reaction. The form of carbon is also important to the intensity of the reaction. Purer and less-structured carbon materials tend to react more readily than more structured carbon materials. Carbon powder is more reactive than graphite, and both are more reactive than paraffin.

One of the goals of this work is to determine if the ISTD process can be implemented at the SDA given the waste types and conditions that exist there. The implementability of ISTD at the SDA must answer the question of whether or not the waste can be heated without the threat of uncontrolled exothermic reactions occurring in the waste. Nitrates alone must reach fairly high temperatures (i.e., greater than 310°C [590°F]) to decompose. Nitrates with chlorinated organics and oil can react when heated. The reaction is exothermic and occurs after most of the chlorinated organics have been volatilized. The testing suggests the temperature for initial reaction is approximately 425°C (797°F). Nitrates with cellulose (paper) react exothermally at about 230°C (446°F). In the Energetic Materials Research and Testing Center test, the reaction showed signs of being a deflagration but not an explosion. Results of testing indicate that there is potential for uncontrolled exothermic reactions. The potential for exothermic reactions must be addressed if ISTD is to be considered at the SDA. As a result, ISTD should not be considered in the SDA at the INL Site.

5. DATA ANALYSIS AND INTERPRETATION—IN SITU GROUTING

In situ grouting may be used to provide structural support to the cap, to immobilize contaminants in the waste, or to facilitate retrieval of waste. The testing discussed here addresses the first two applications. The structural support of the cap may be in the form of individual columns or a monolith. Immobilization of contaminants will be in the form of a monolith placed in regions of interest. This testing includes waste and surrogates, depending on the type of testing conducted.

5.1 Evaluate Durability of Grouted Waste

All of the tests in this section used surrogate without radionuclides.

The testing covered in this section of the report focuses on the physical aspects of durability, such as compressive strength, porosity, and hydraulic conductivity. Grout durability is discussed in more detail by Hanson et al. (2005).

5.1.1 Compressive Strength

Loomis et al. (2003) conducted a series of compressive strength tests using GMENT-12, TECT HG, U.S. Grout, and Saltstone. These tests found that none of the grouts could accept greater than 50 wt% soil loading, not greater than 12 wt% organic sludge, and not greater than 25 wt% nitrate salt surrogates. WAXFIX was tested under the same conditions and all of the grouts with ISTD-treated organic sludge were tested. The unconfined compressive strength of WAXFIX, GMENT-12, U.S. Grout, TECT HG, and several Portland cement-based formulations[h] was evaluated at several waste loadings. For a detailed description of the methods and procedures used in the compressive strength testing, see Appendix B. The grouts were least tolerant of the organic sludge surrogate and most tolerant of soil.

h. The Portland cement formulations were only tested with soil since that was the waste form of interest for these formulations.

An unconfined compressive strength of 250 psi[i] was set as the minimum acceptable strength for a grout column in this study. The limit was based on the minimum strength that would result in a free-standing column that could be readily handled during the leach and physical testing required. Compressive strength does not directly correlate to the ability of a grout to immobilize contaminants, but it can provide a qualitative indication of the overall integrity of the grout-waste mixture.

Two possible methods for injecting the grout were considered. One method would involve injecting grout in a series of offset injection holes to form a contiguous monolith. An alternate method would be to create individual columns at predetermined offsets that would not interconnect. While an unconfined compressive strength less than 250 psi may be acceptable for providing structural support to the cap if the grout is placed to form a monolith, a higher compressive strength would be needed if only individual columns were used to support a cap. A higher compressive strength is also more conservative than the Environmental Protection Agency and Nuclear Regulatory Commission standards for landfill covers (Shaw and Weidner 1996, Loomis et al. 2003). The grouting study (Stephens 2004) recommended a compressive strength of 1,200 psi for grouts where noncontiguous individual columns are placed out to support a cap. All of the grouts tested have sufficient unconfined compressive strength for serving as a monolith at some loading of each of the waste forms studied (see Figures 42 through 47). However, the presence of organic sludge greatly reduces the ability of the grouts to form stable monoliths at loading greater that 9 wt%. In addition, WAXFIX would not be appropriate if it were being injected to form a support for a cap and the grout was not injected to form a contiguous monolith since the compressive strength is typically less than 1,000 psi. Results presented in figures are an average of five samples with a confidence interval of 95%.

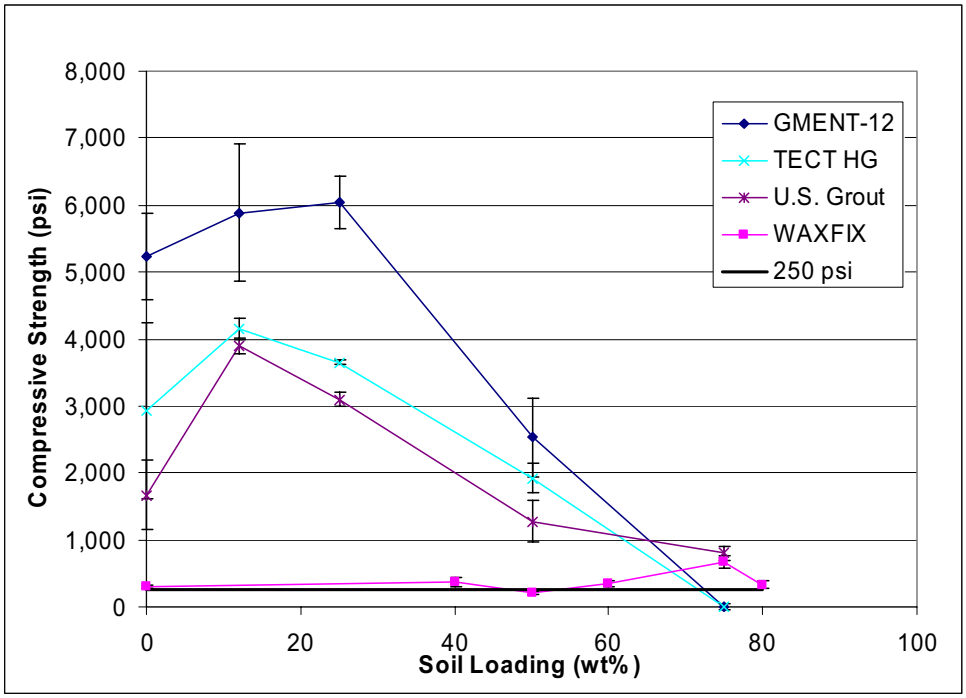

Figure 42. Compressive strength of grout and grout-soil mixtures.

[i] The Code of Federal Regulations specifies the compressive strength of grouted materials for waste disposal be 50 psi (10 CFR 61). The Nuclear Regulatory Commission specifies a minimum compressive strength of 60 psi and recommends that the compressive strength of hydraulic cements be 3.45 MPa (500 psi) or greater (NRC 1991).

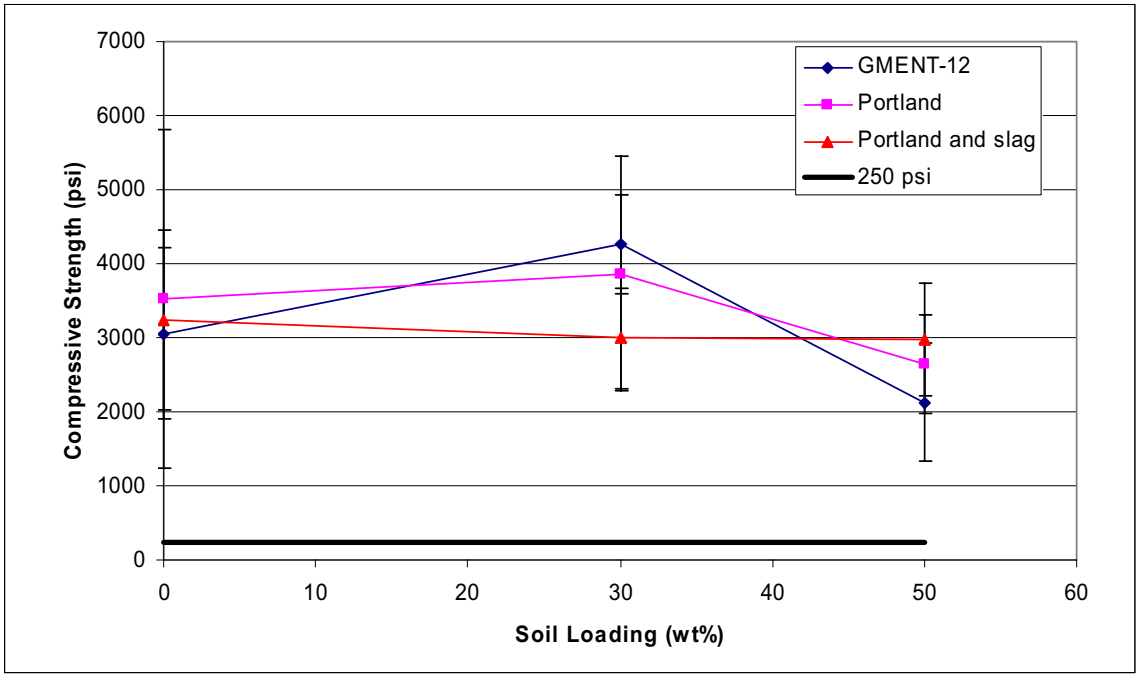

Figure 43. Compressive strength for grout and grout-soil mixtures.

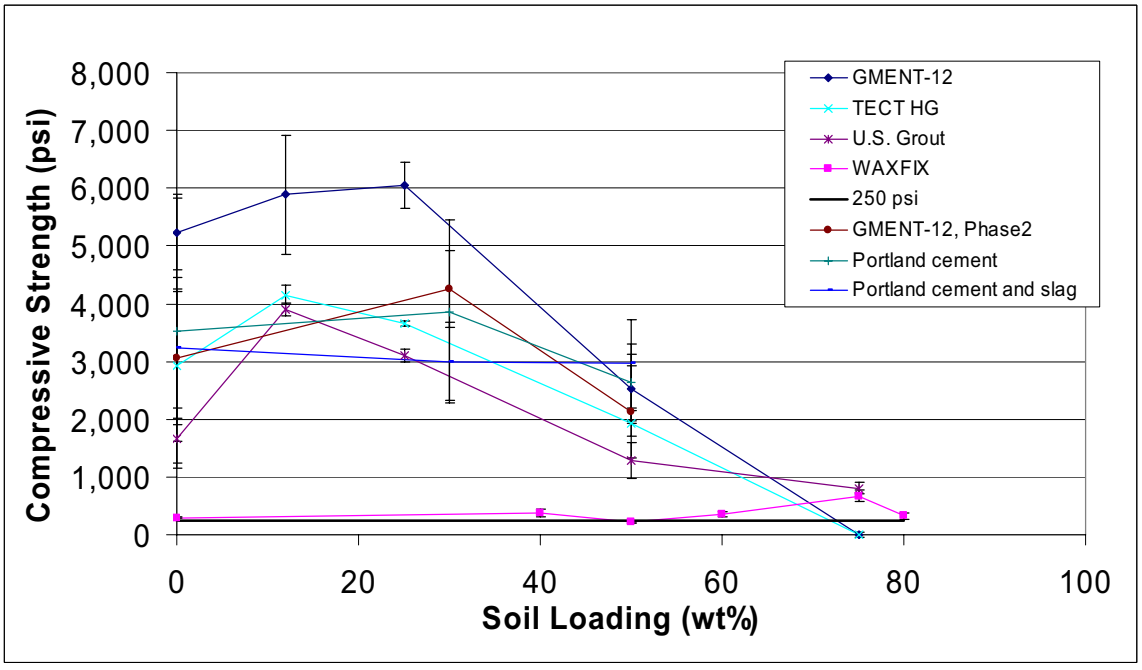

Figure 44. Combined results for initial and phase 2 testing of compressive strength for grout and grout-soil mixtures.

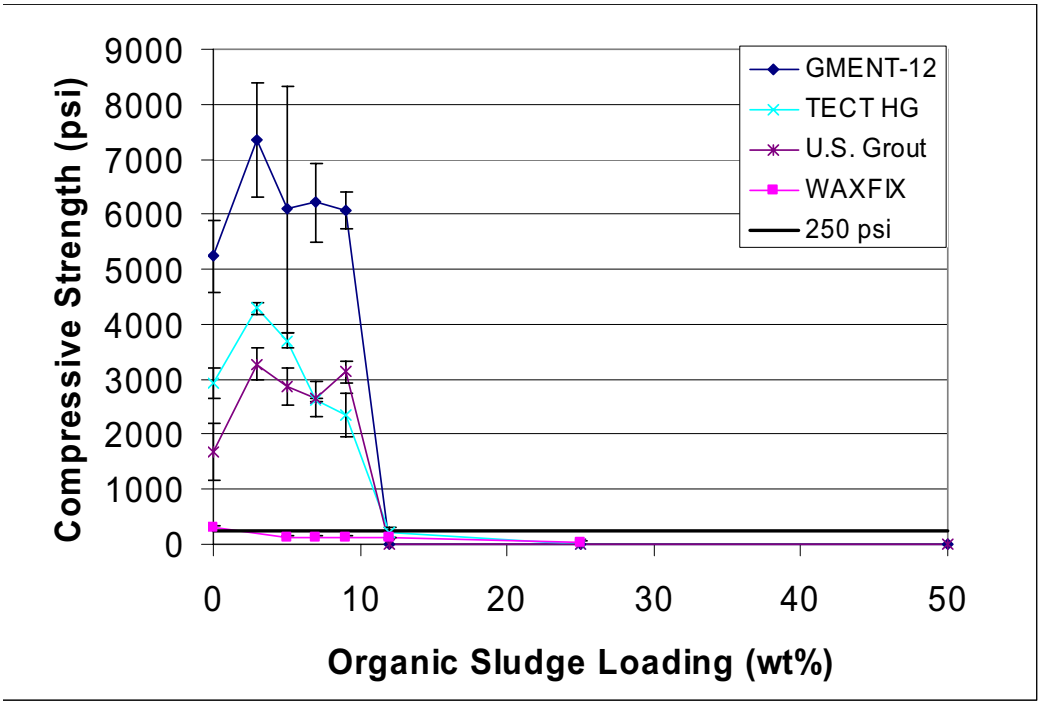

Figure 45. Compressive strength of organic sludge and grout mixtures.

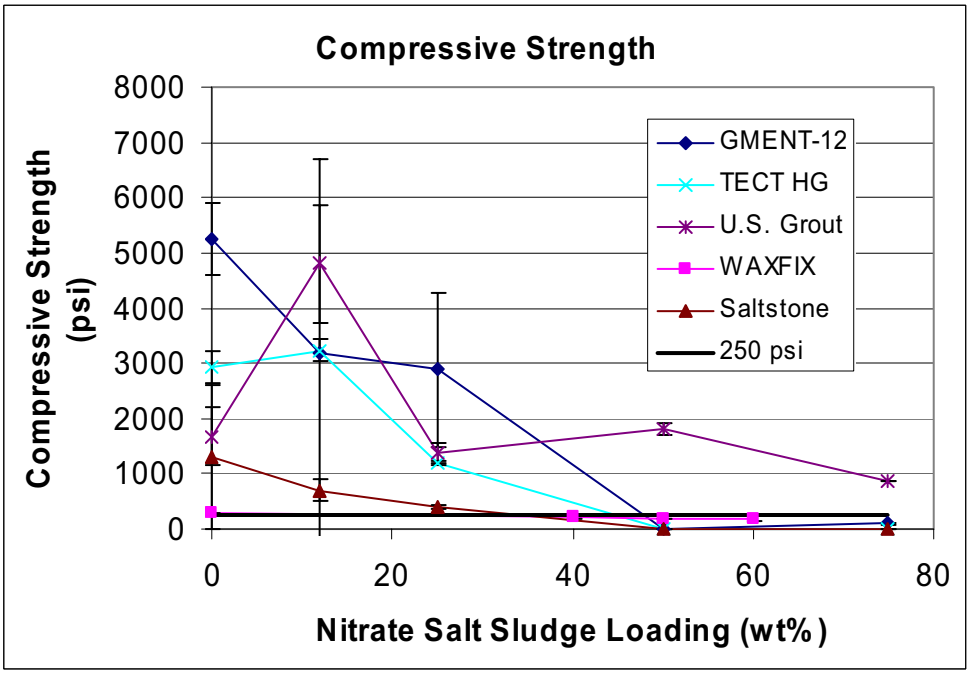

Figure 46. Compressive strength with nitrate salt sludge surrogate.

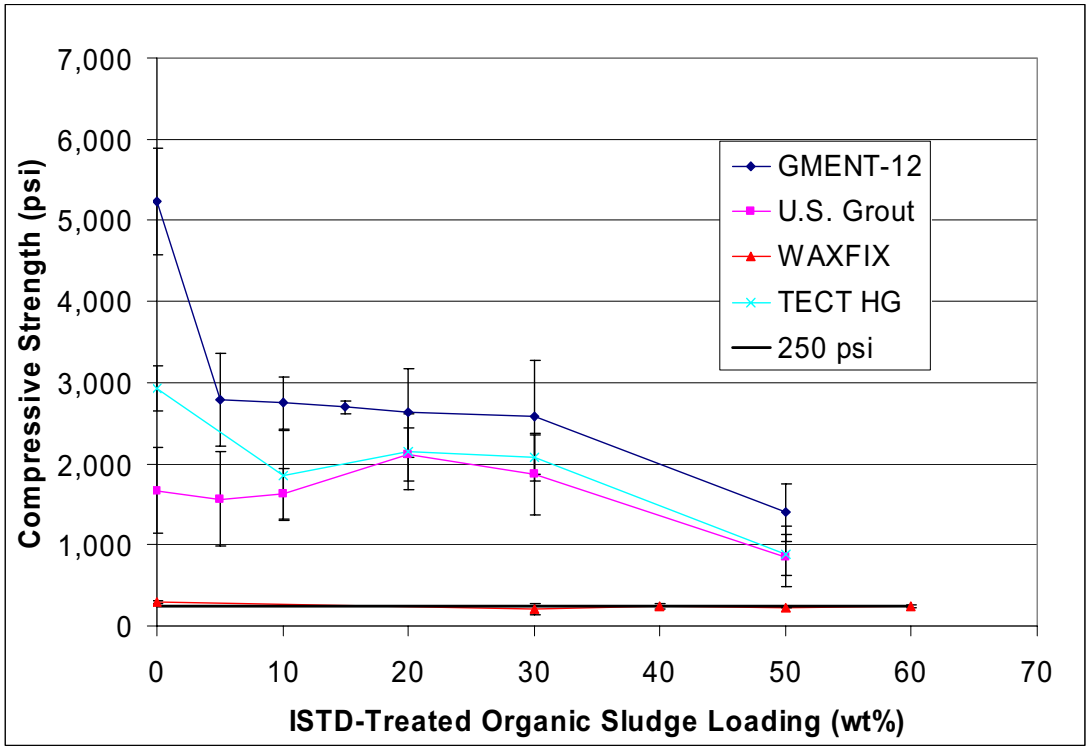

Figure 47. Compressive strength with ISTD-treated organic sludge as a surrogate.

Results of compressive-strength testing were used to select waste loadings for the remaining testing presented in this report. The waste loading was selected so that:

- All grouts could be tested at the same waste loading in subsequent tests
- The 250-psi compressive-strength criterion was met for all grouts and waste
- Waste loading would challenge performance of the grout.

Waste loadings for each type of waste were set independently. The loadings selected for each waste form are listed in Table 2.

Table 2. Waste loadings used for hydraulic conductivity, porosity, and leach studies.

	Selected Loading (wt%)	
Waste	WAXFIX	Cementitious Grouts[a]
Soil[b]	70	50
Organic sludge surrogate	9	9
Inorganic sludge surrogate	30, 60	30, 60
Pad A nitrate salt surrogate	60	12
ISTD-treated organic sludge surrogate	60	50
Organic sludge waste	5, 9, 15	5, 9, 15

Table 2. (continued).

Waste	Selected Loading (wt%)	
	WAXFIX	Cementitious Grouts[a]
Pad A nitrate salt waste	25, 50	25, 50
ISTD-treated organic sludge waste	9	9

a. Nonproprietary Portland-cement-based grouts are included in this column

b. This waste type includes the Portland-cement-based grouts used in the second set of testing.

Based on results of the compressive-strength tests, all of the grouts produce samples with compressive strengths that exceed the baseline limit of 250 psi when tested as neat grout. In fact, all of the cementitious grouts (GMENT-12, TECT HG, U.S. Grout, Portland cement, and Portland cement with blast furnace slag) exceeded 3,000 psi compressive strength for neat grout. The WAXFIX samples had compressive-strength values much less (about 300 psi), which was expected.

When the grouts were mixed with soil, they could easily be mixed at a 50-50 ratio and still maintain good compressive strength. For WAXFIX, the composition could be as high as 70 wt% soil and actually produce the highest compressive strength for the WAXFIX samples. The organic sludge had the greatest negative impact on the compressive strength of the grouted samples. The grouts could only handle waste loadings in the 9 to 10 wt% waste composition before they lost their ability stay together as a cohesive sample. When the grouts were mixed with nitrate salts, the U.S. Grout performed the best compared to the other cementitious grouts and was able to be mixed at a 50-50 ratio and still maintain good compressive strength, while the other grouts could only handle 30 wt% nitrate salts.

When the organic sludge was ISTD treated before grouting, it significantly improved the ability of grouted waste to form cohesive samples at higher waste loadings. While the untreated organic sludge could only be mixed at a composition of 9 to 10 wt%, the ISTD-treated organic sludge could be mixed at a composition of 50 wt% and have a compressive strength greater than 250 psi. From a practical standpoint, not only can more waste be mixed with the grout after it is thermally treated, but there is less waste to be grouted, there is more void space available to accept the grout, and the resultant waste form has a higher compressive strength.

5.1.2 Porosity

The porosity test measured connected and surface pores accessible to water. Porosity is an indicator for water accessibility. Higher porosities suggest greater accessibility of water to the interior of the grouted mass. Water is primarily a concern for physical durability if there is the potential for freeze-thaw cycling of grouted material. Freeze-thaw cycling is not expected to be a major concern for the grouted waste over long term, since a cap would be placed over the existing waste, thus placing it below the winter freeze depth (Pittman 1989). However, water accessibility would be a concern for contaminant migration. Appendix C provides descriptions of the methods and procedures used in porosity testing. The addition of grout to the soil lowered the porosity relative to soil alone, except with U.S. Grout. The heavy black line in Figure 48 represents the porosity of soil at the INL Site. The porosity of WAXFIX was lower than that of the cementitious grouts (see Figure 48 and is consistent with the macroencapsulation properties of WAXFIX. WAXFIX contains pores, but they are not as likely to be connected as the pores in the crystalline cementitious grouts.

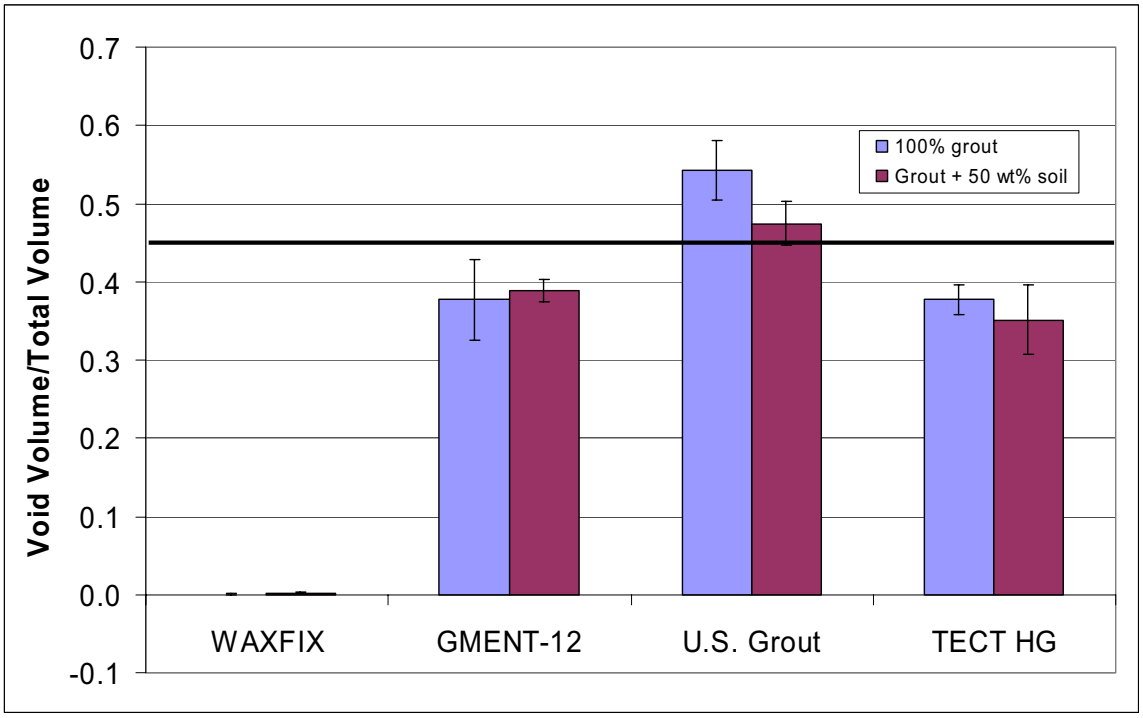

Figure 48. Porosity of grouted surrogate forms containing 0 and 50 wt% soil.

A second series of porosity tests used GMENT-12 (a proprietary grout formulation) and nonproprietary grout formulations, in particular Portland Type II and Portland Type II mixed with blast furnace slag at a concentration of 50 wt% grout plus 50 wt% blast furnace slag. Porosity was measured using the grouts just mentioned as neat grout and the grout with soil mixed at concentrations of 30 wt% soil and grout with 50 wt% soil.

Figure 49 shows the relationship among the three grout formulations tested. Error bars represent the 95% confidence interval. Measured values of porosity for surface soil from the INL Site range from approximately 0.4 to 0.5 volume fraction and are represented by the line shown in Figure 49 at 0.45 volume fraction. Porosity of GMENT-12 was significantly lower than Portland-cement-based grout in all cases. As waste loading increased, porosity of GMENT-12 increased. The reverse was true for the Portland-cement-based grouts. The Portland-cement-based grout and the Portland with slag mixture had higher porosity when tested as neat grout than at the 30 or 50 wt% soil loading.

In almost all cases, mixing grout with soil results in a reduction in porosity compared to soil alone (as represented by the solid black line in Figure 49), which should result in a decrease in water movement through the waste. Thus, grouting the waste should reduce the porosity and result in a reduction in contaminant mobility. Only when the U.S. Grout (Figure 48) was added to the soil did the porosity increase rather than decrease relative to the soil alone.

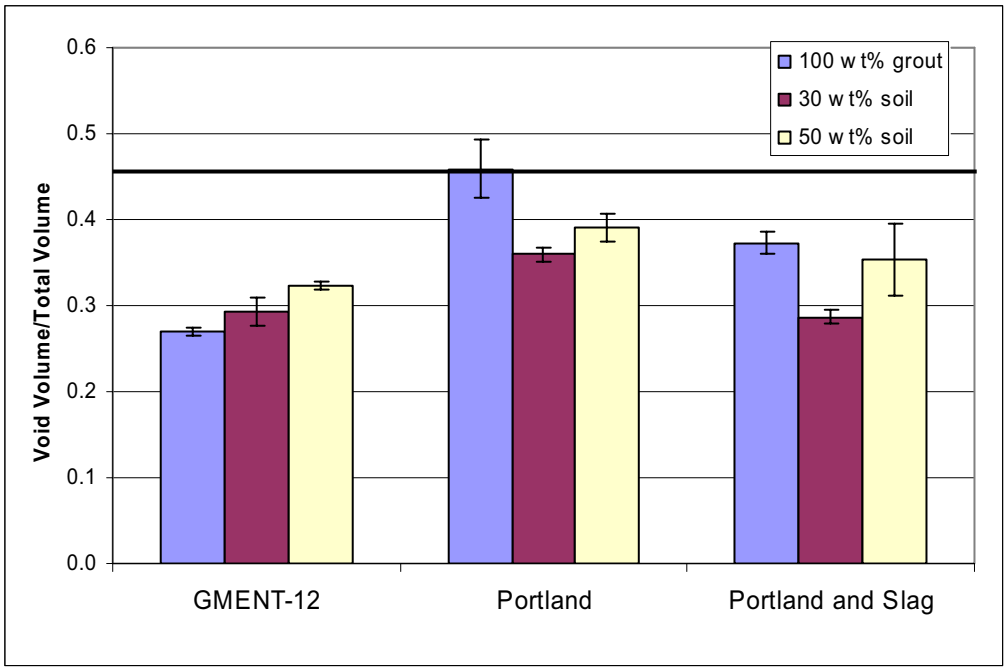

Figure 49. Porosity of grouted surrogate forms.

5.1.3 Hydraulic Conductivity

Hydraulic conductivity was measured for neat WAXFIX and with surrogate. Previous testing of cementitious grouts with the same surrogates is shown in Figures 50 and 51. (In Figure 50, data for WAXFIX are from current testing. Data are for remaining grouts from prior studies [Loomis et al. 2003]. Error bars represent 95% confidence intervals. WAXFIX was tested at 70 wt% soil and 60 wt% nitrate salt surrogate. Appendix D provides detailed information on the methods and procedures used in the hydraulic conductivity testing. WAXFIX as a neat material had the lowest hydraulic conductivity of all grouts tested, which is consistent with the porosity data collected on these materials. Similar to porosity, hydraulic conductivity is not a direct measure of durability. Materials with high hydraulic conductivities will let water move through them more easily than materials with low hydraulic conductivities. The presence of water in materials can lead to removal of grout and waste materials through dissolution or promotion of freeze-thaw cycle-based fracturing. Soil at the INL Site usually has a hydraulic conductivity on the order of 1E-04 cm/second (McElroy and Hubbell 1990). All of the grouts measured had hydraulic conductivities on the order of 1E-07 cm/second or less, significantly less than that of soil.

GMENT-12 performed as well as neat grout with soil and with organic sludge added but performed much worse than the other grouts when mixed with nitrate salts. U.S. Grout performed comparably with the other grouts, except with organic sludge where it had a significantly higher hydraulic conductivity.

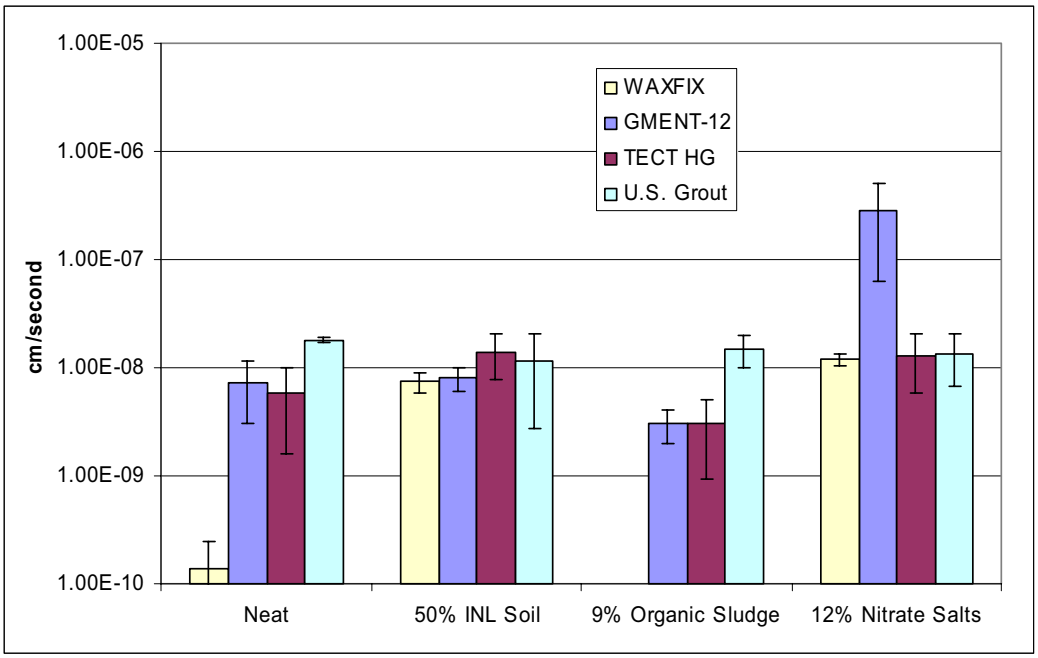

Figure 50. Hydraulic conductivity of four grouts (WAXFIX, GMENT-12, TECT HG, or U.S. Grout), neat (100 wt% grout), and mixed with one of three surrogates (soil, organic sludge surrogate, or nitrate salt surrogate) (WAXFIX was tested at 70 wt% in soil and 60 wt% in nitrate salts).

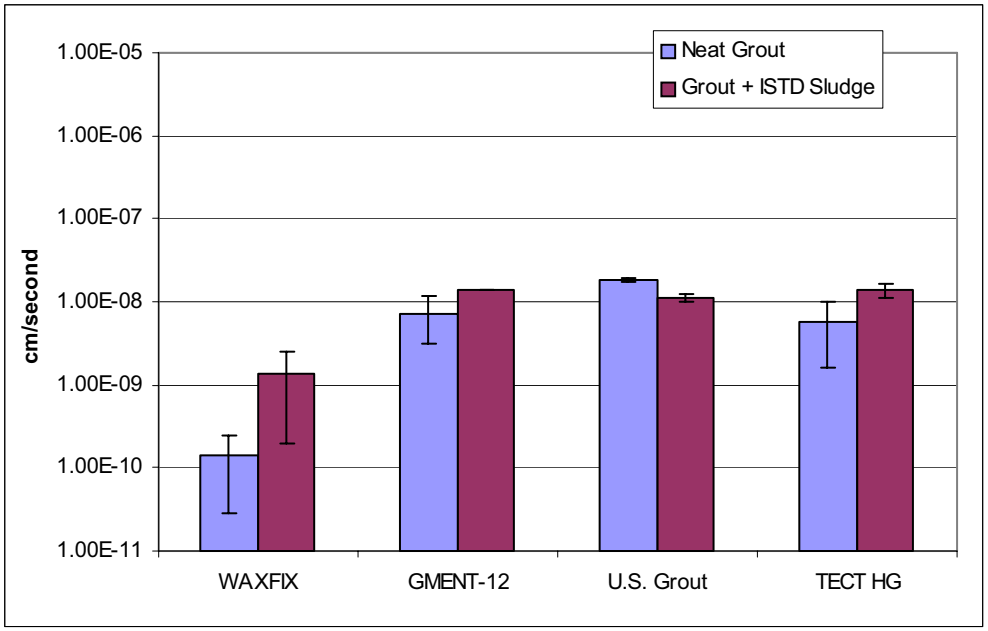

Figure 51. Hydraulic conductivity of four grouts (WAXFIX, GMENT-12, TECT HG, or U.S. Grout), neat (100 wt% grout), and mixed with ISTD-treated organic sludge surrogate.

A second series of hydraulic conductivity tests used GMENT-12 (a proprietary grout formulation) and nonproprietary grout formulations, in particular Portland Type II and Portland Type II mixed with blast furnace slag at a 50-50 ratio. The hydraulic conductivity was measured using neat grout, grout with 30 wt% soil, and grout with 50 wt% soil.

Figure 52 shows the relationship among the three grout formulas tested. Error bars represent the 95% confidence interval. Based on these results, all of the grouts behaved satisfactorily with respect to hydraulic conductivity, but the Portland-cement-based grouts mixed with blast furnace slag provide the greatest reduction in hydraulic conductivity at 50 wt%, while the GMENT-12 and Portland-cement-based grout performed equally well with 30 wt% soil added.

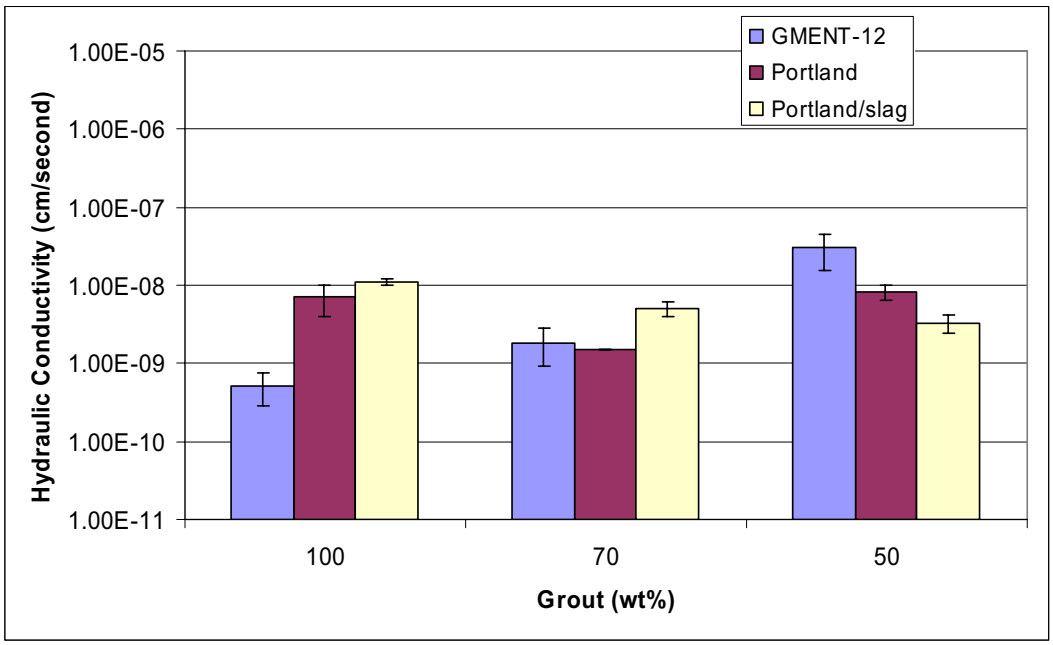

Figure 52. Hydraulic conductivity measurements for GMENT-12, Portland cement, and Portland cement with slag at 0, 30, and 50 wt% of soil in grout.

The results using the Portland cement and Portland cement with slag compared similarly to the tests performed using GMENT-12, TECT HG, and U.S. Grout, except that Portland-cement-based grout with blast furnace slag had lower hydraulic conductivity values than any of the grouts tested when mixed with 50 wt% soil.

5.1.4 Durability Summary

For each grout tested, adding waste materials generally decreased compressive strength and increased hydraulic conductivity and porosity of the grouts compared to neat grout samples; however, the porosity and hydraulic conductivity of grouted waste samples, even at 50 wt% waste loading, were lower than the ungrouted waste. This indicates that grouting should result in a reduction in water movement through the waste. Adding grout to waste in the subsurface should decrease the average porosity and hydraulic conductivity of the waste zone and will improve the structural stability of the waste zone.

5.2 Develop Data to Support Contaminant Transport Modeling for Treated Waste Forms

Tests in this section used surrogates spiked with radionuclides or waste containing radionuclides (iodine, carbon, technetium, uranium, plutonium, americium, and neptunium as appropriate for the specific surrogate) as described.

One of the potential uses of ISG is reducing mobility of contaminants of interest. Grouts can reduce contaminant mobility by macroencapsulation, chemical interaction, or a combination of the two processes. For the grouts used in this study, WAXFIX reduces mobility primarily by macroencapsulation, and the cementitious grouts reduce mobility through a combination of chemical interaction and macroencapsulation.

Mobility of selected radionuclide contaminants was measured using the abbreviated ANS leaching protocol. These tests were performed according to the ANS leach test. These tests were specified in Section 4.3.3.9 of Yancey et al. (2003). The abbreviated protocol was selected to decrease the overall length of the studies (1 week instead of 3 months). The leach index measured by this testing represents the log of the inverse of the effective diffusivity of the contaminant. The lower the leach index, the higher the effective diffusivity and the more mobile the contaminant is under the conditions tested. The cylindrical samples specified in ANS 16.1 have dimensions of 5 × 10 cm (2 × 4 in.). Here, 2 × 3-cm (0.75 × 1.2-in.) samples were prepared to conserve valuable actinide tracers and to decrease radiological control concerns. The calculations for leach indices account for sample dimensions, so that the results reported here are comparable to those that would have been measured for 5 × 10-cm (2 × 4-in.) samples. The purpose of the leach test is to provide a basis for comparison among various grout and waste mixtures. The test is a very short-term measurement compared to the leach processes that will occur over hundreds and thousands of years, but ANS 16.1 does provide an estimate of contaminant mobility in a waste form. The leach index, rather than effective diffusivity, is used to compare results because it is less sensitive to small changes in measured values, and a 99.9% confidence interval is applied to the value to ensure a conservative approach in terms of seeing differences among waste forms.

Four sets of ISG experiments were performed: non-TRU, non-TRU Part 2, TRU, and ISTD of TRU. The radionuclides of interest for the non-TRU experiments were I-129, C-14, Nb-94, and Tc-99. Niobium was not included in testing because of its limited availability and high cost. This first set of tests was conducted using WAXFIX and the proprietary grouts that had been previously field-tested (GMENT-12, TECT HG, U.S. Grout). A nonradioactive isotope of iodine, I-127, was used for non-TRU Part 2 testing to simplify the analysis for C-14. Part 2 testing was conducted using nonproprietary grout (commercially available Portland cement) tested by itself and mixed with slag, thiosulfate, fly ash, or other combinations. The radionuclides of interest for the TRU and ISTD of TRU experiments were uranium, plutonium, americium, and neptunium. These tests were conducted using only the proprietary grouts.

5.2.1 Leaching—In Situ Grouting of Nontransuranic Part 1

Non-TRU experiments examined a single type of waste form: soil spiked with the radionuclides I-129, C-14, and Tc-99. Non-TRU waste in the SDA is expected to consist of debris in soil. Contaminated soil was selected as a representative waste form for testing grout. The first set of experiments included the following grout formulations: TECT HG, WAXFIX, GMENT-12, U.S. Grout, and Saltstone.

The results of the leach tests for the non-TRU Part 1 samples are shown in Figure 53. Each sample contained 50 wt% soil, which was spiked with Tc-99 (5.00E+05 pCi/g), I-129 (2.00E+04 pCi/g), and C-14 (4.13E+04 pCi/g). The samples were performed in triplicate; the mean and a confidence interval of

99.9% about the mean are presented in Figure 53 (see Table O-3 in Appendix O for additional detail on leach index values).

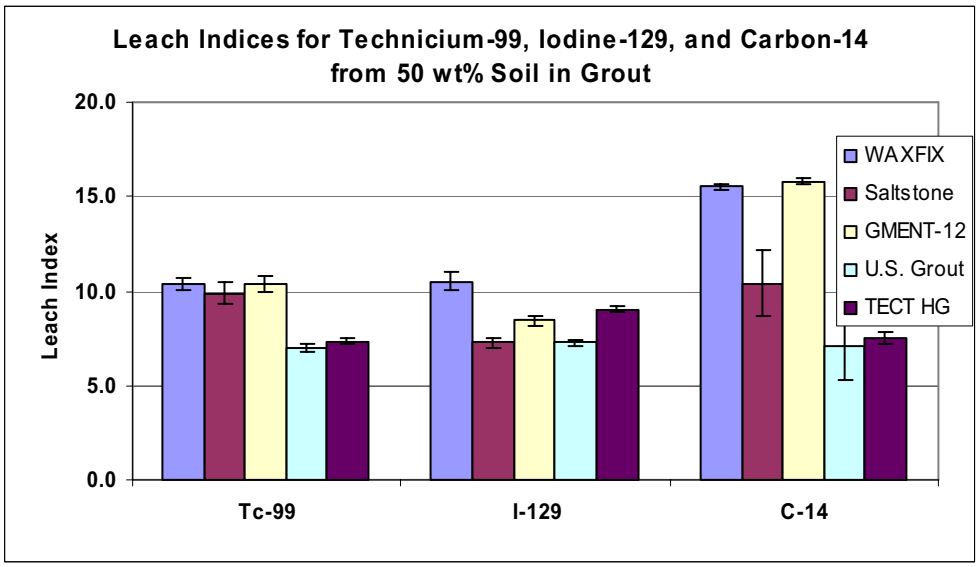

Figure 53. Nontransuranic Part I testing, mean leach index for grout containing 50 wt% soil spiked with technetium-99, iodine-129, neptunium, and carbon-14.

In Part 1, for technetium, the leach indices for WAXFIX, Saltstone, and GMENT-12 are statistically higher than those for U.S. Grout and TECT HG. For iodine, the leach indices for WAXFIX are statistically higher than the other grouts. For carbon, the leach indices for WAXFIX and GMENT-12 are statistically higher than those for Saltstone, U.S. Grout, and TECT HG. WAXFIX and GMENT-12 are the only two grouts that exhibit higher leach indices for all three radionuclides.

For Non-TRU Part 1 tests, WAXFIX and GMENT-12 had the highest leach indices overall. Saltstone performed well on T-99, and TECT HG performed well on I-29, but overall, WAXFIX and GMENT-12 were the best at reducing the leachability of radionuclides tested.

5.2.2 Leaching—In Situ Grouting of Nontransuranic Part 2

The initial set of non-TRU ISG testing focused on proprietary grout formulations. Since three of the original grouts were Portland-cement-based formulations, the performance of nonproprietary Portland cement was explored. The non-TRU Part 2 experiments included the following grout formulations (see Appendix A for detailed recipes):

- Portland cement
- Portland cement with fly ash
- Portland cement with slag
- Portland cement with fly ash and sodium thiosulfate
- Portland cement with slag and sodium thiosulfate.

For Part 2 of non-TRU testing, each sample contained 50 wt% soil, which was spiked with Tc-99 (4.42E+04 pCi/g), I-128 (4.22E+05 pCi/g), and C-14 (7.94E+05 pCi/g). The samples were performed in

triplicate. The mean and a confidence interval of 99.9% about the mean are presented in Figure 54 (see Table P-6 in Appendix P for additional detail on leach index values.

For Tc-99 in the nonproprietary grout formulations (see Figure 54), Portland cement with slag and thiosulfate was statistically higher than Portland cement with fly ash or Portland cement with fly ash and thiosulfate. Considering all of the grout formulations, WAXFIX, GMENT-12, Portland cement, Portland cement with slag, Portland cement with slag and thiosulfate, and Portland cement with fly ash and thiosulfate were statistically higher than U.S. Grout. Portland cement, Portland cement with slag and thiosulfate, and Portland cement with fly ash and thiosulfate were also statistically higher than TECT HG.

For iodine in the nonproprietary grout formulations (see Figure 54), Portland cement and Portland cement with fly ash and thiosulfate were higher than Portland cement with slag and Portland cement with fly ash. Considering all of the grout formulations, WAXFIX was higher than U.S. Grout, Portland cement with slag, and Portland cement with fly ash.

For C-14 in the nonproprietary grout formulations (see Figure 54), Portland cement with slag and Portland cement with slag and thiosulfate were statistically higher than Portland cement, Portland cement with fly ash, or Portland cement with fly ash and thiosulfate. Considering all of the grout formulations, there appear to be three groups. The highest leach index values were shown by WAXFIX, GMENT-12, Portland cement with slag, and Portland cement with slag and thiosulfate. The lowest leach index values were shown by U.S. Grout and TECT HG. Saltstone, Portland cement, Portland cement with fly ash, and Portland cement with fly ash and thiosulfate showed leach index values between the other two groups.

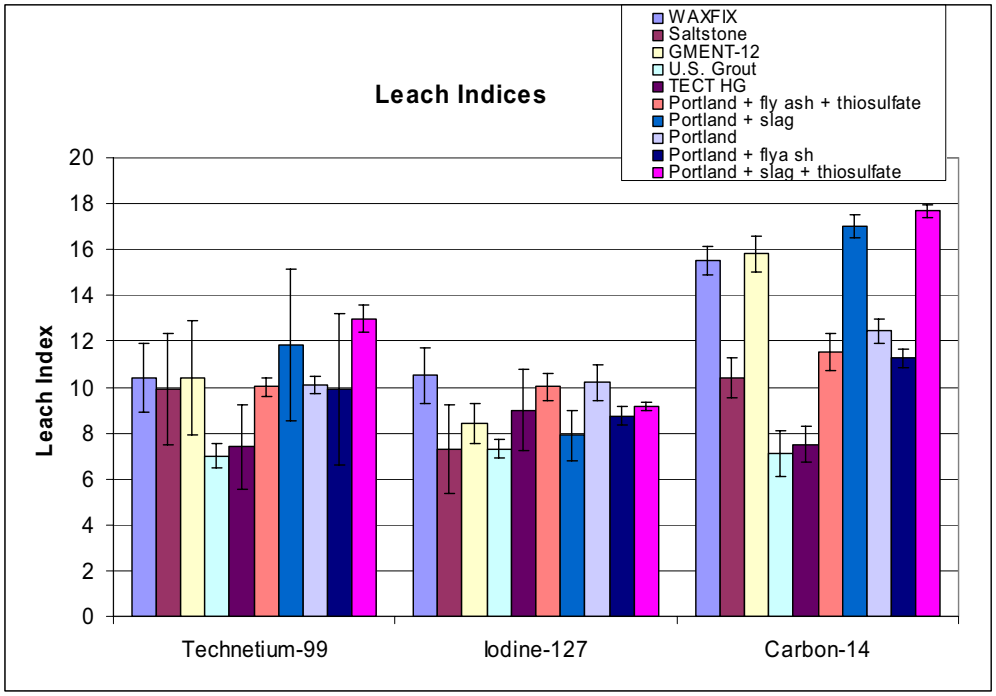

Figure 54. Nontransuranic Parts 1 and 2 testing, mean leach index for grout containing 50 wt% soil spiked with technetium-99, iodine-127, and carbon-14.

Considering all three elements and ten grout formulations, U.S. Grout and TECT HG generally showed the lowest leach index values, while WAXFIX, GMENT-12, Portland cement with slag, and Portland cement with slag and thiosulfate generally showed the highest leach index values. Based on the

leach index, Portland cement with slag, Portland cement with slag and thiosulfate, WAXFIX, and GMENT-12 would be the best and essentially equal choices for immobilization of C-14, Tc-99, and I-129 in soil. If cost also is considered, then the Portland cement with slag likely will be the best choice if a well-characterized and consistent source of slag is available.

5.2.3 Leaching—In Situ Grouting of Transuranic Waste

In situ grouting of TRU contaminants evaluated four grout formulations (U.S. Grout, GMENT-12, WAXFIX, and TECT HG) with three surrogates: soil, organic sludge, and inorganic sludge and two types of waste: organic sludge and Pad A nitrate salts. Surrogates were spiked with four radionuclides: plutonium, uranium, americium, and neptunium. Actinide concentrations in surrogates were selected based on isotope and median concentration data in Blackwood and Hoffman (2004). Concentrations of natural uranium, Pu-239, Np-237, and Am-241 were used, as close as possible to the medians specified, but with considerations for both instrument detection limits for leachate analysis and radiological control practices. The concentrations of radionuclides in the leachate were measured with inductively coupled plasma-mass spectrometry (ICP-MS). The following radionuclides were present in the soil (after spiking) at the concentrations shown: 1,381 nCi/g (22.6 ppm) of plutonium; 2,216 nCi/g (0.65 ppm) of americium; 152 nCi/g (210 ppm) of neptunium; and 808 ppm of uranium. Organic sludge surrogate was spiked with the following concentrations of radionuclides: 1,411 nCi/g (23.1 ppm) of plutonium; 2,262 nCi/g (0.66 ppm) of americium; and 825 ppm of uranium. Organic sludge collected from the SDA at the INL Site was analyzed and found to have the following concentrations of radionuclides: 1.60 ppm of plutonium, 0.265 ppm of americium, 0.0156 ppm of neptunium, and 130 ppm of uranium. Two batches of inorganic sludge surrogate were prepared and spiked with the following ratios of radionuclides:

- Batch 1—1,383 nCi/g (22.6 ppm) of Pu; 2,219 nCi/g (0.65 ppm) of americium; 152 nCi/g (210 ppm) of neptunium; and 809 ppm of uranium

- Batch 2—1,345 nCi/g (22.0 ppm) of plutonium; 2,157 nCi/g (0.63 ppm) of americium; 2 nCi/g (2.8 ppm) of neptunium; and 800 ppm of uranium.

The surrogate was mixed with each of the grout types at a composition of 30 wt%.

While the surrogates were spiked with radionuclides well above the 100-nCi/g limit for TRU waste and above the concentrations measured in the organic sludge waste for most grouts, waste loadings, and TRU radionuclides, the concentrations of radionuclides (plutonium, uranium, americium, or neptunium) in the leachate were below the detection limit of the ICP-MS machine. The detection limit of ICP-MS is different for each radionuclide and varies for a specific radionuclide from day to day. When two-third or more of data fell below the detection limit, the detection limit was used to calculate the leach index. This approach provided a worst-case estimate for the minimum values of leach index, which is worst case with respect to estimating mobility of contaminants.

5.2.3.1 Surrogate—Soil. The results for 30 wt% soil in grout are presented in Figure 55. The only data with some detectable results were for uranium and neptunium from WAXFIX (see Table M-21 in Appendix M for additional detail on leach index values); therefore, Figure 55 should be read as showing the minimum value of the leach index for each set of samples tested. While the leach indices for neptunium appear to be higher than that for the other radionuclides, no conclusions can be drawn, since all of the data represent detection limits rather than measurements.

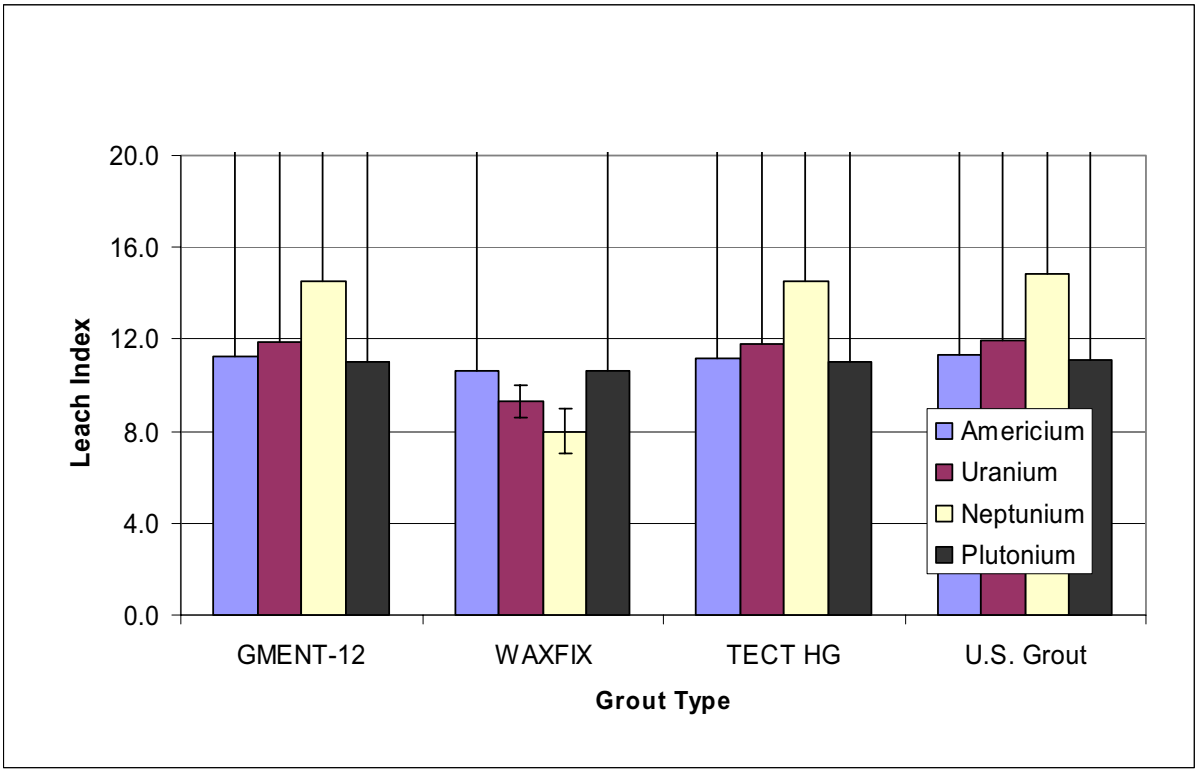

Figure 55. Leach indices for americium, uranium, neptunium, and plutonium from 30 wt% Idaho National Laboratory soil and grout.

5.2.3.2 Surrogate—Organic Sludge. Organic sludge surrogate was mixed with grout at 5 and 9 wt% loadings of sludge surrogate in grout. These loadings were selected to correlate with the maximum loadings that could be achieved and still have a cohesive sample as determined by compressive strength tests. The results for 5 and 9 wt% organic sludge surrogate in grout are presented in Figures 56 and 57, respectively. Neptunium was not added to the organic sludge surrogate (see Table M-21 in Appendix M for additional detail on leach index values). For these graphs, all of the values were below detection; therefore, Figure 55 should be read as showing the minimum value of the leach index for each set of samples tested. While leach indices for americium appear to be lower than those for plutonium across the grout formulations, no conclusions can be drawn since all of the data represent detection limits rather than measurements.

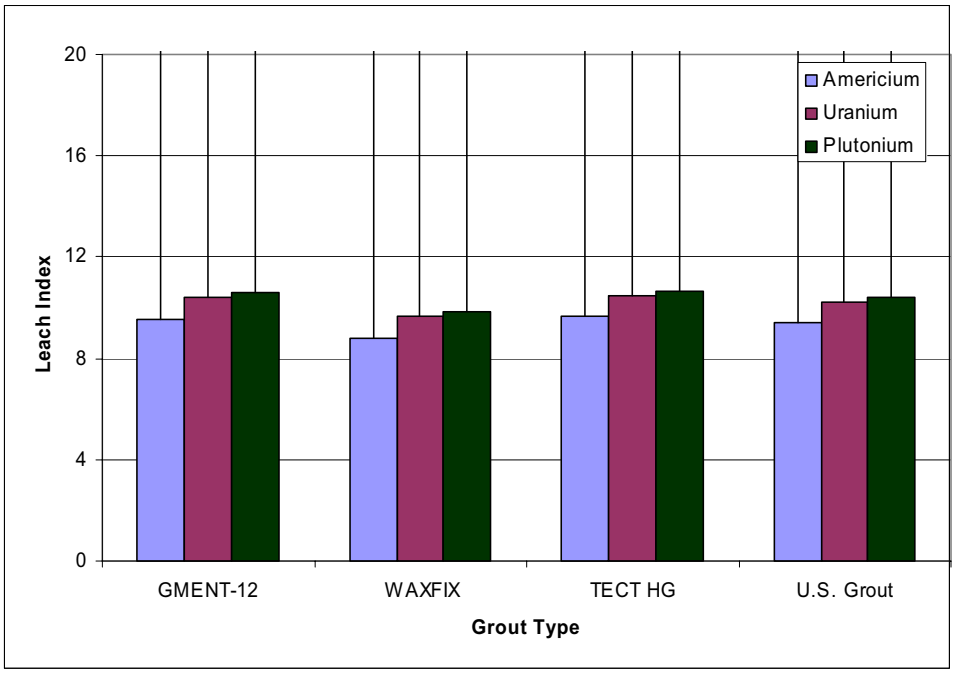

Figure 56. Leach indices for americium, uranium, and plutonium from 5 wt% organic sludge surrogate and grout.

Less than 2/3 of the measured values in Figure 56 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

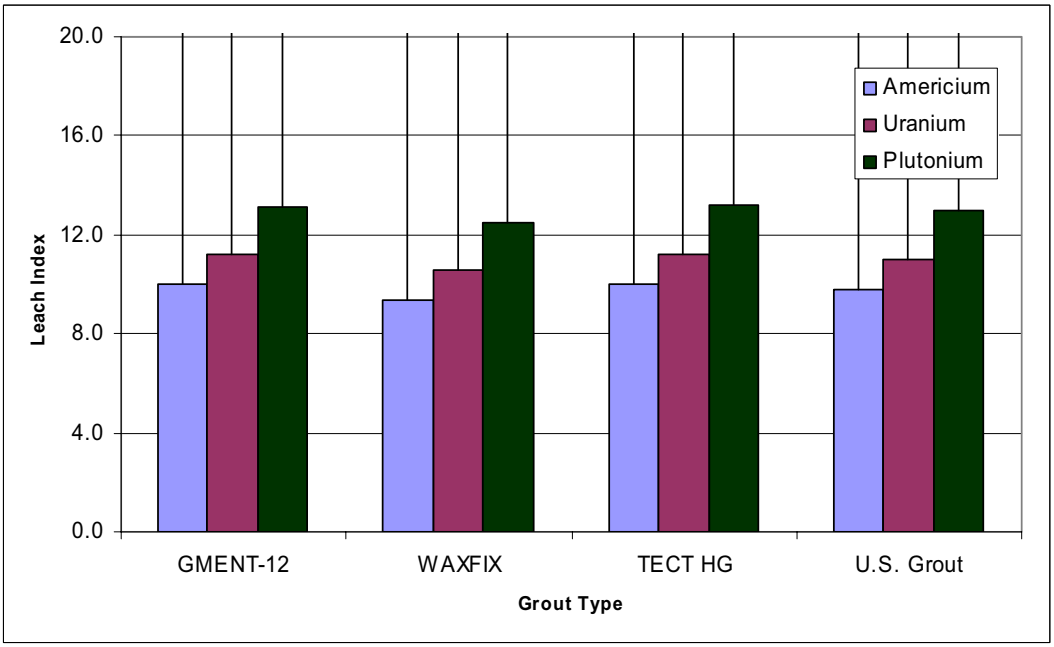

Figure 57. Leach indices for americium, uranium, and plutonium from 9 wt% organic sludge surrogate and grout.

Less than 2/3 of the measured values in Figure 57 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

Because all of the results came back as nondetectable, it is not possible to determine a difference between the grouts tested; however, this shows again that grouting the waste is a promising way to reduce the leachability of the contaminants, especially if grout can be added to a waste loading of 5 to 9 wt% relative to organic sludge.

5.2.3.3 Surrogate—Inorganic Sludge. The results for 30 and 60 wt% inorganic sludge surrogate in grout are presented in Figures 58 and 59, respectively. In all cases, the inorganic sludge was mixed, the radionuclides were added in a slurry mixture, and the mixture of inorganic sludge and radionuclides was then oven-dried overnight. This dried mixture was then grouted with each of the grouts. In some cases, additional water was added to the cementitious grouts to aid in the mixing process. This was not needed with the WAXFIX (see Appendix M for details). WAXFIX will mix easily with dry or moist soils or wastes, but in the presence of free liquids, the WAXFIX may not distribute evenly in the soil and could compromise the integrity of the monolith. For these tests, most data were nondetect. Where radionuclides were detected, values were close to the nondetect values. The leach index values presented in Figures 58 and 59 (see Table M-21 in Appendix M for additional detail on leach index values) with one-sided error bars should be read as showing the minimum value of the leach index for the set of samples tested. The samples where radionuclides were detected have two-sided error bars. The leach index for uranium in WAXFIX was lower than the leach index for the other grouts at 30 and 60 wt% loadings. No other statistically significant differences were observed.

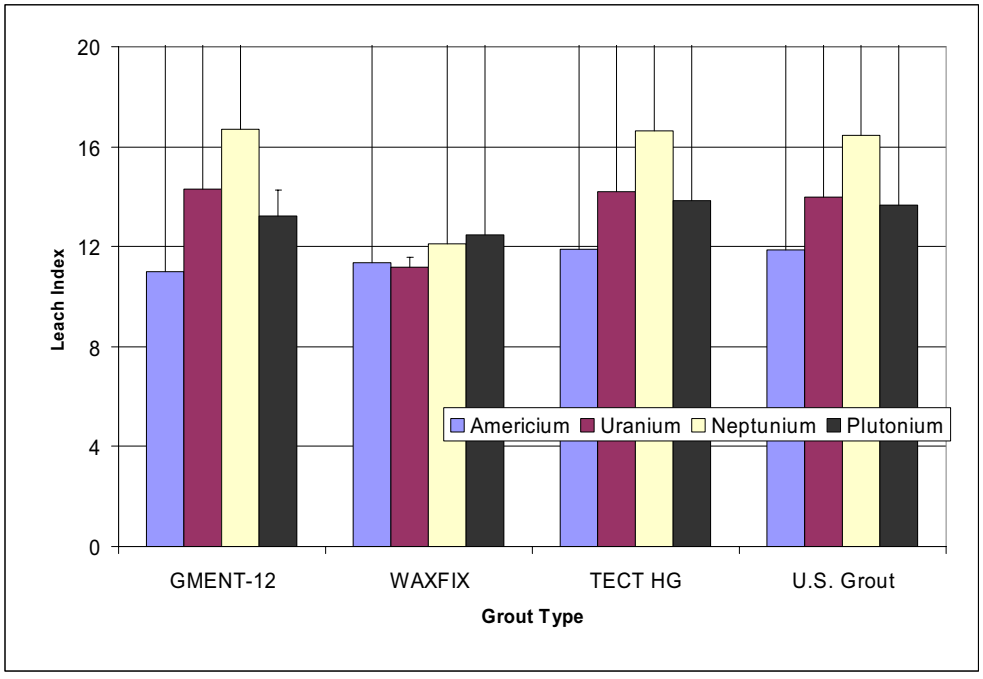

Figure 58. Leach indices for grout and inorganic sludge at 30 wt% waste loading.

Less than 2/3 of the measured values in Figure 58 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

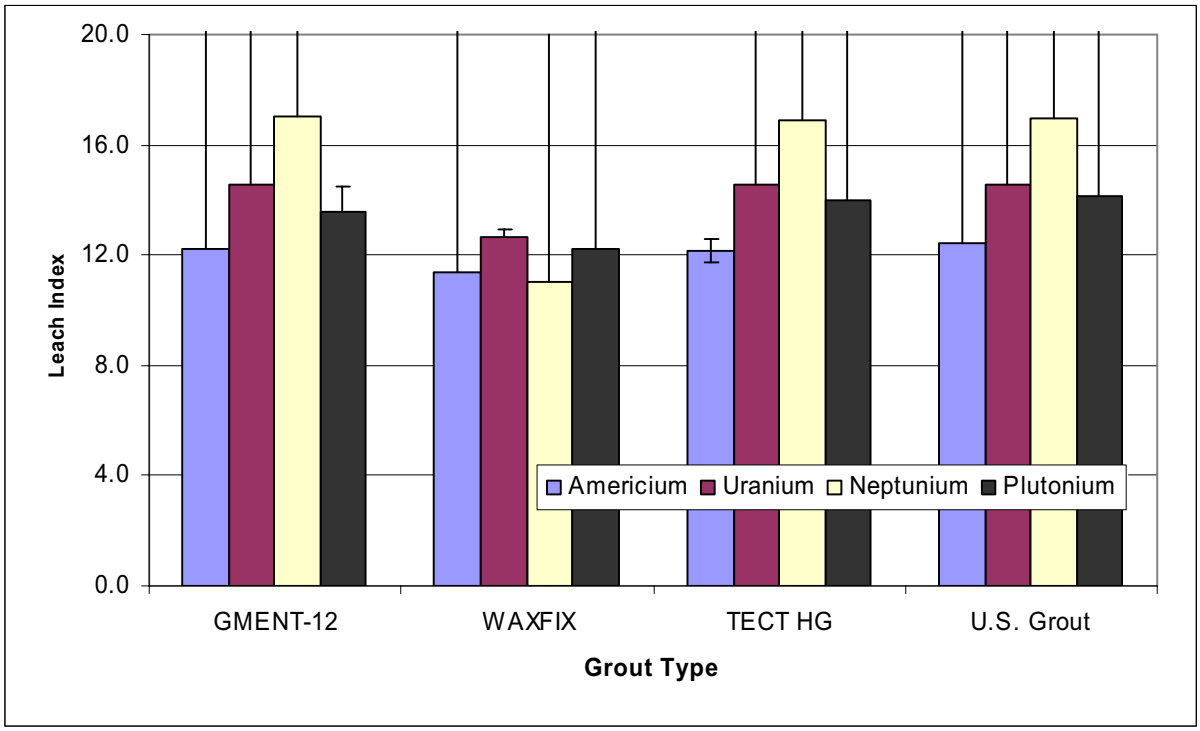

Figure 59. Leach indices for grout and inorganic sludge at 60 wt% waste loading.

Less than 2/3 of the measured values in Figure 59 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

Comparing results from the 30 and 60 wt% inorganic sludge surrogate loadings in grout, the radionuclide concentrations in the leachate from the 60 wt% samples were still mostly nondetect, leading to unchanged leach index values.

5.2.3.4 Waste—Pad A. Waste loadings for Pad A waste were selected to correlate with the maximum loadings achieved during compressive strength testing. The results for 12 wt% Pad A nitrate salt samples are presented in Figure 60 (see Table M-21 in Appendix M for additional detail on leach index values). For these tests, most data were nondetect. The leach index values presented in Figure 60 with one-sided error bars should be read as showing the minimum value of the leach index for the set of samples tested. The samples where radionuclides were detected have two-sided error bars. The leach index for uranium in WAXFIX was lower than the leach index for the other grouts. No other statistically significant differences were observed.

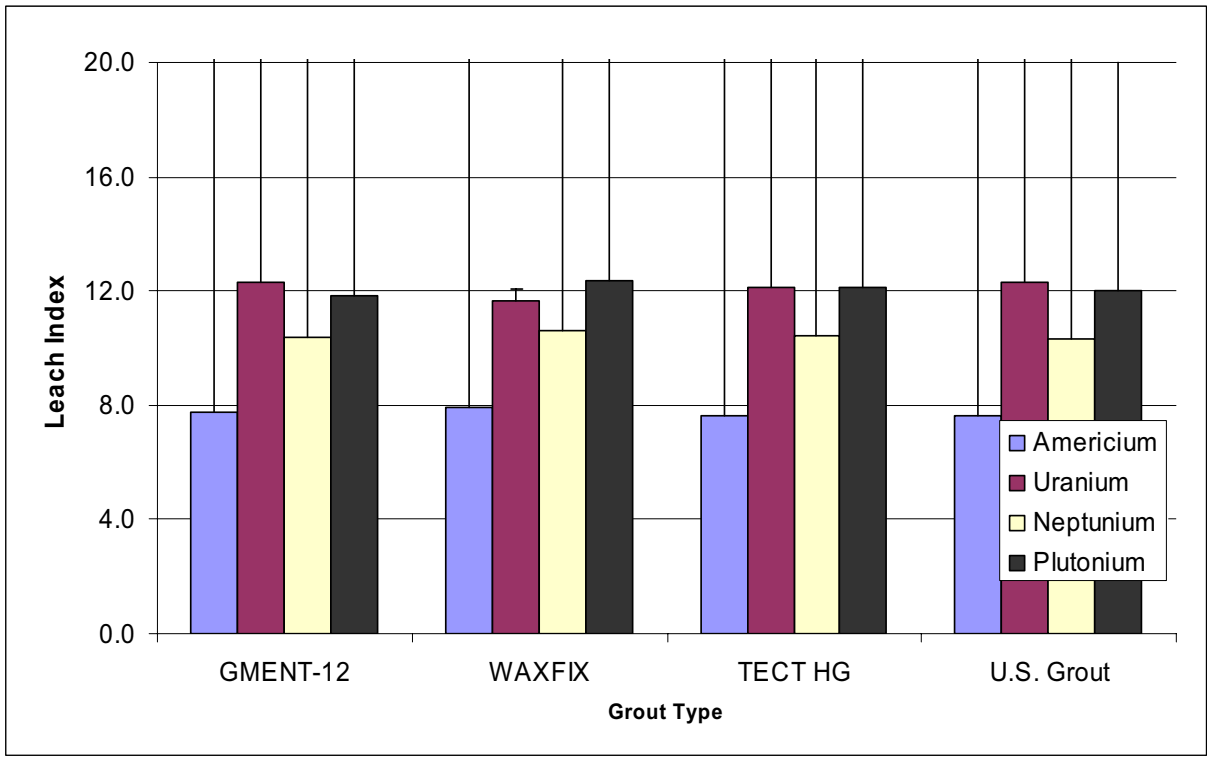

Figure 60. Leach indices from nitrate salt sludge at 12 wt% (Pad A waste).

Less than 2/3 of the measured values in Figure 60 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

With respect to leach indices, all of the grouts performed equally well at reducing the leachability of the COCs when treating Pad A waste.

5.2.3.5 Waste—Organic Sludge. Organic sludge waste retrieved from Pit 9[j] was combined with grout at 5, 9, and 15 wt% loadings of sludge waste in grout. Loomis et al. (2003) found that the grouts tested could only achieve about a 12 wt% waste loading of organic sludge and still maintain a cohesive sample. Based on those results, the waste loadings of 5, 9, and 15 wt% were chosen for the leach testing. The results for 5, 9, and 15 wt% organic sludge waste loadings in grout are presented in Figures 61, 62, and 63, respectively (see Table M-21 in Appendix M for additional detail on leach index values). For these graphs, only the uranium was detected in the leach solutions from the WAXFIX samples. The leach index values presented with one-sided error bars should be read as showing the minimum value of the leach index for the set of samples tested. The samples for which radionuclides were detected have two-sided error bars.

j. The organic sludge waste used in these tests was retrieved from Pit 9 during the Glovebox Excavator Method Project (DOE-ID 2004).

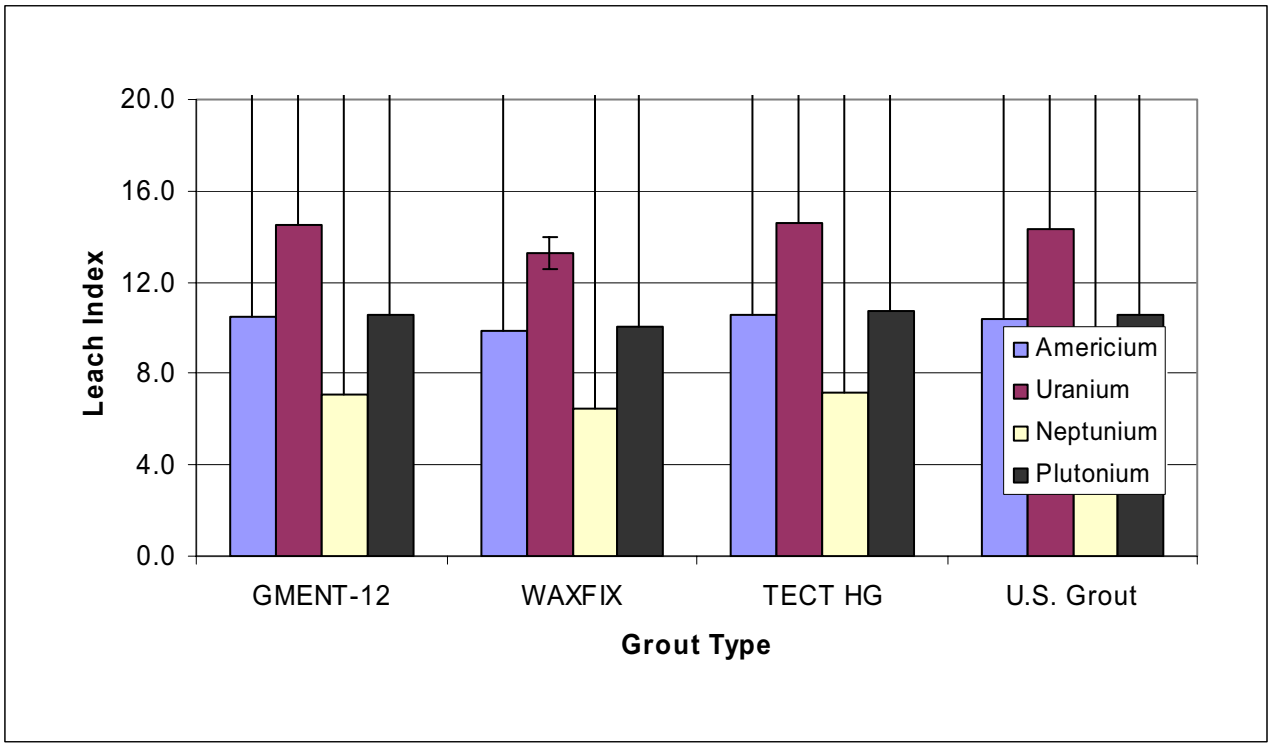

Figure 61. Leach indices for americium, uranium, and plutonium from 5 wt% organic sludge waste and grout.

Less than 2/3 of the measured values in Figure 61 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

While all but one sample were nondetect at 5 wt% organic sludge waste in grout, uranium was detected in all grouts with 9 wt% organic sludge waste, but only in two of the grouts (GMENT-12 and WAXFIX) with 15 wt% organic sludge waste. At 9 and 15 wt%, the leach index for WAXFIX was significantly lower than for TECT HG and U.S. Grout. No other differences were observed among the radionuclides or grouts.

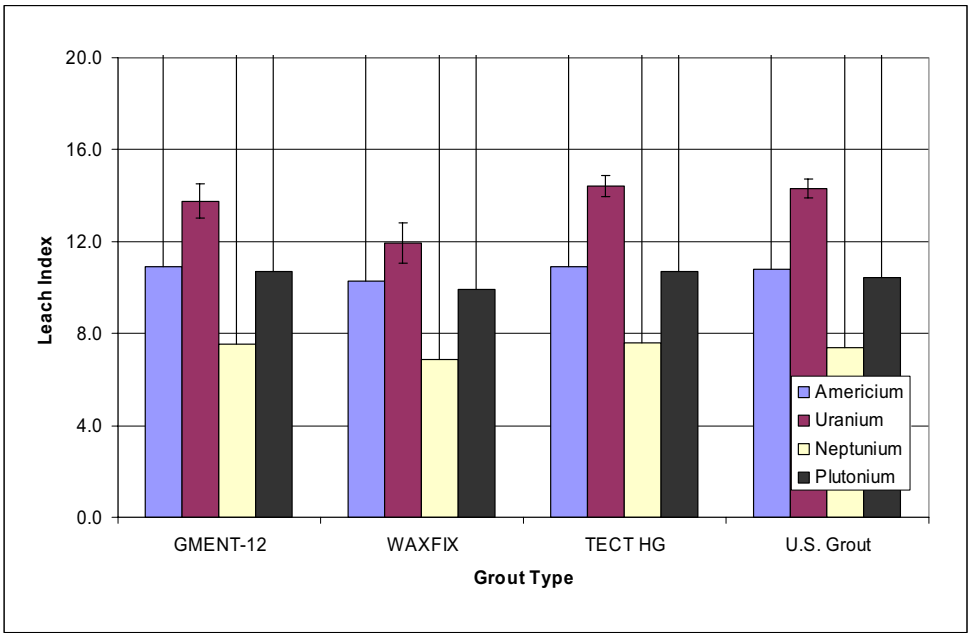

Figure 62. Leach indices for americium, uranium, and plutonium from 9 wt% organic sludge waste and GMENT-12.

Less than 2/3 of the measured values in Figure 62 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

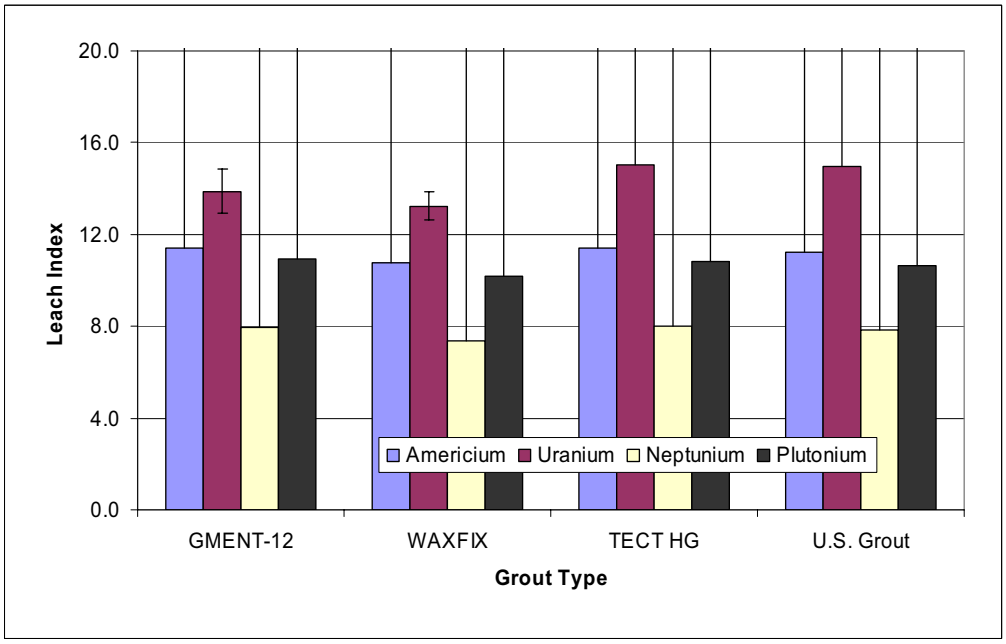

Figure 63. Leach indices for americium, uranium, neptunium, and plutonium from 15 wt% organic sludge waste and grout.

Less than 2/3 of the measured values in Figure 63 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

5.2.4 Leaching—In Situ Grouting of ISTD

Organic sludge surrogate and waste were thermally treated with ISTD at 450°C (842°F) and mixed with each of the grout types at a loading of 9 wt%. The results vary with the radionuclide (see Appendix N for details). Data from samples of organic sludge surrogate and waste not treated with ISTD before grouting (grouted at the same loading of 9 wt%) (see Appendix M for details) are included in the graphs for comparison.

Figures 64 through 67 show the leach indices, by radionuclide, for grouted organic sludge surrogate and waste that have been pretreated with ISTD and without pretreatment. Where no radionuclide was detected in the leachate, the leach index was calculated using the detection limit for each sample measurement. The leach indices calculated represent minimum values, because most measured concentrations in the leachate were below the detection limit. The actual leach indices should be greater than or equal to the values presented in Figures 64 through 67. The leach index values presented with one-sided error bars should be read as showing the minimum value of the leach index for the set of samples tested. The samples where radionuclides were detected have two-sided error bars; the error bars shown in the figures indicate the 99.9% confidence interval.

For the ISTD-treated and then grouted organic sludge surrogate, the concentrations of plutonium and americium were nondetectable (defined here as below detection limits in two-third or more of the samples). In the same samples, uranium was nondetectable except for the samples grouted with WAXFIX; the leach index for uranium was significantly lower for WAXFIX than for the other grouts tested.

For the ISTD-treated and then grouted organic sludge waste, the concentrations of plutonium and americium were nondetectable in the leach solutions. In the same samples, uranium and neptunium were both nondetectable, except for the samples grouted with WAXFIX. The leach index for uranium and neptunium was slightly less for WAXFIX than for the minimum leach index for the other grouts.

In the grouted organic sludge surrogate samples, the concentrations of plutonium, americium, and uranium were nondetectable in the leach solutions. In grouted organic sludge waste samples, the concentration of uranium was detected in the leach solutions from GMENT-12, WAXFIX, and TECT HG, but not from U.S. Grout. Plutonium, americium, and neptunium were not detected in the leach solutions from any of the grouts tested.

No statistical difference was observed among the grouts or wastes for americium, plutonium, or neptunium, even though the concentration of radionuclides in the ISTD pretreated samples was higher than the concentration of radionuclides in the samples without ISTD pretreatment. Uranium was detected in leachate from 9 wt % organic sludge surrogate with GMENT-12 and TECT HG, but the leach index was not statistically different from the other grouted samples or forms of organic sludge. Uranium was detected in leachate from WAXFIX samples prepared with ISTD pretreated organic sludge surrogate, ISTD pretreated organic sludge waste, and organic sludge waste. WAXFIX, unlike the cementitious grouts, works by macroencapsulation (coating) alone. The samples tested were quite small, so they had a relatively large surface-area-to-volume ratio. Any particle of radionuclide that ended up uncoated at the surface would be available for leaching. In the subsurface, a grouted region would extend beyond the expected volume containing the radionuclides to minimize this effect. Uranium also was detected in the leachate from samples prepared with all four grouts with organic sludge waste but not from samples

prepared with ISTD pretreated organic sludge waste. This suggests that removal of organic compounds from waste before grouting can improve the ability of grout to immobilize radionuclides. In all grout and organic sludge combinations studied, the mean leach index for uranium was greater than 8, for americium and plutonium greater than 9, and for neptunium greater than 5. Based on the presented leach index values, neptunium is the most difficult to immobilize; however, since neptunium was not detected in the leachate of any of the samples analyzed, the lower leach index reflects the detection limit of the instrumentation used, rather than the mobility of neptunium.

ISTD pretreatment removes most of the organic compounds present in the organic sludge and, therefore, increases the concentration of radionuclides in the sludge sample on a per mass basis. (This concentration effect is only true for the samples being grouted and should not be used to infer that ISTD treatment at the SDA would concentrate radionuclides in the soil.) Since all samples being compared contained 9 wt% of sludge, the ISTD pretreated samples contained more radionuclides per unit mass and less organic compounds than the samples prepared without ISTD pretreatment.

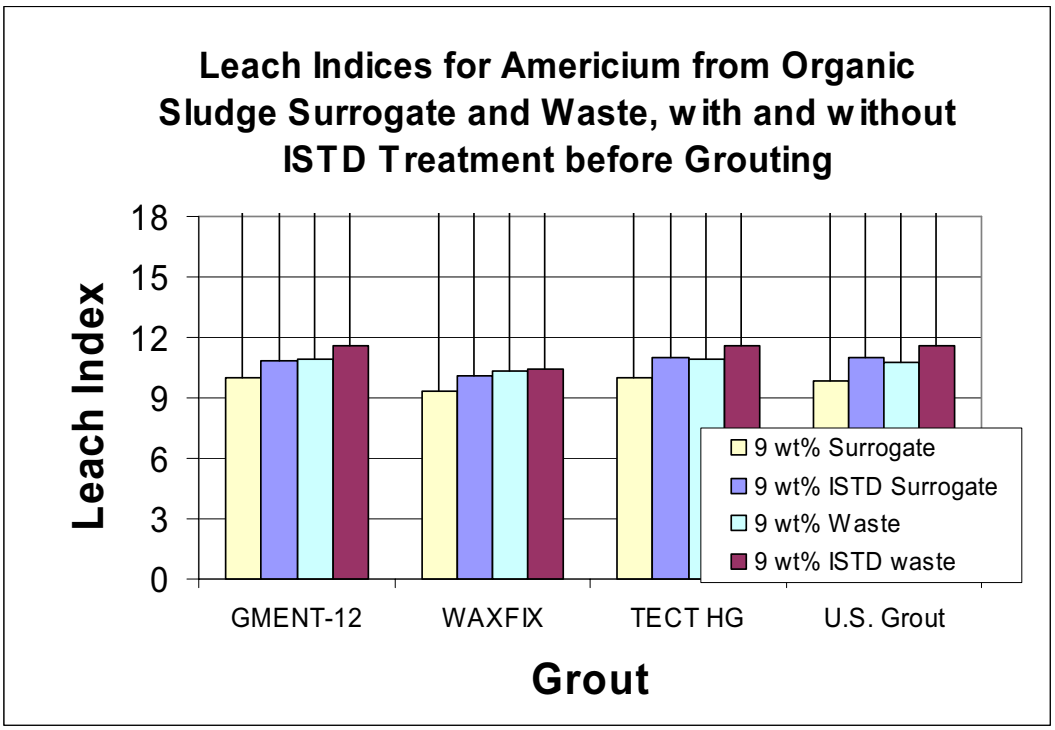

Figure 64. Leach indices for americium for organic sludge surrogate and waste, with and without ISTD treatment at 450°C (842°F) before grouting.

Less than 2/3 of the measured values in Figure 64 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

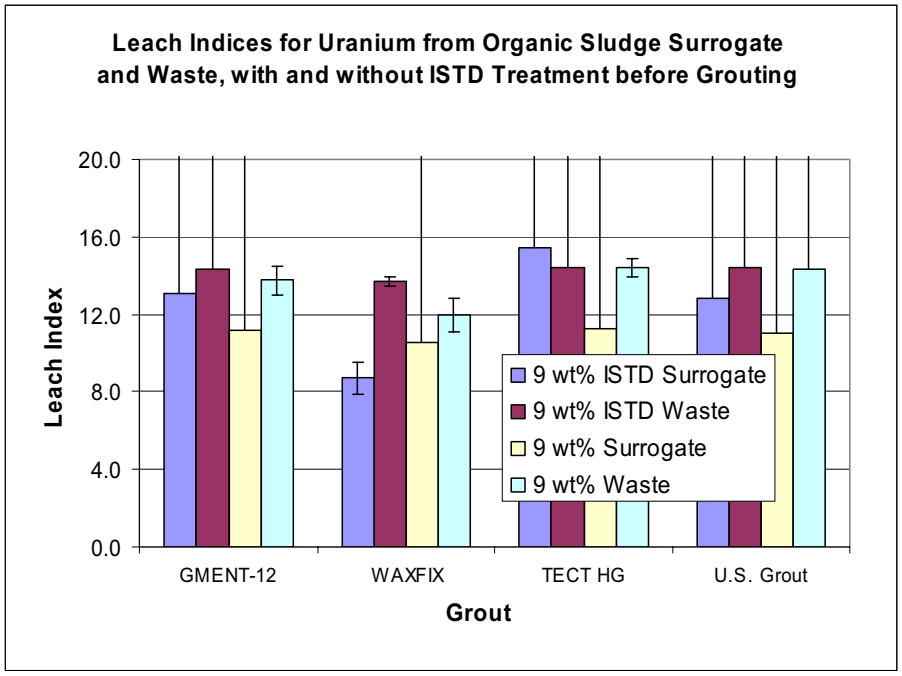

Figure 65. Leach indices for uranium for organic sludge surrogate and waste, with and without ISTD treatment at 450°C (842°F) before grouting.

Less than 2/3 of the measured values in Figure 65 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

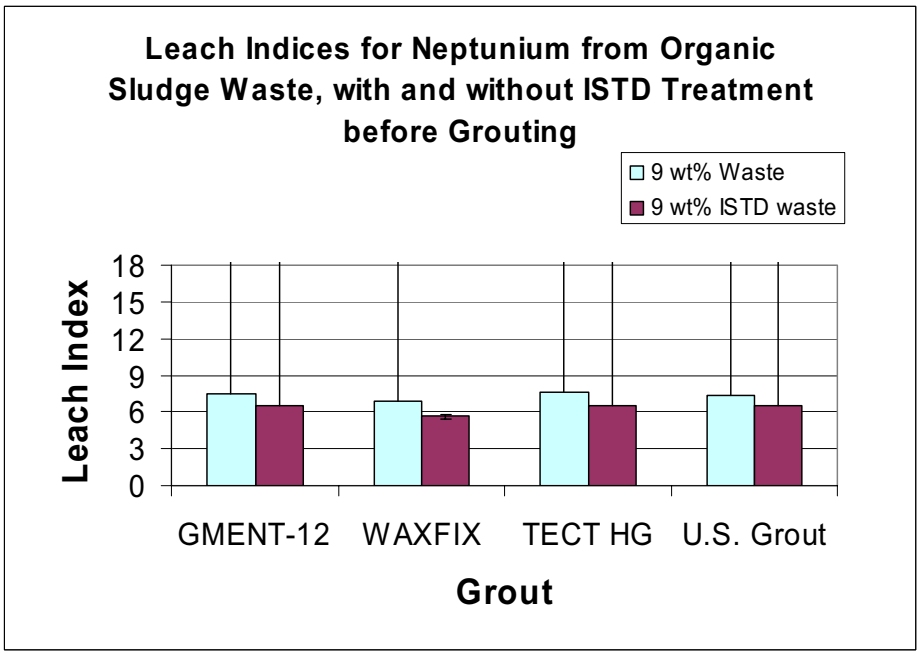

Figure 66. Leach indices for neptunium for organic sludge waste, with and without ISTD treatment at 450°C (842°F) before grouting.

Less than 2/3 of the measured values in Figure 66 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

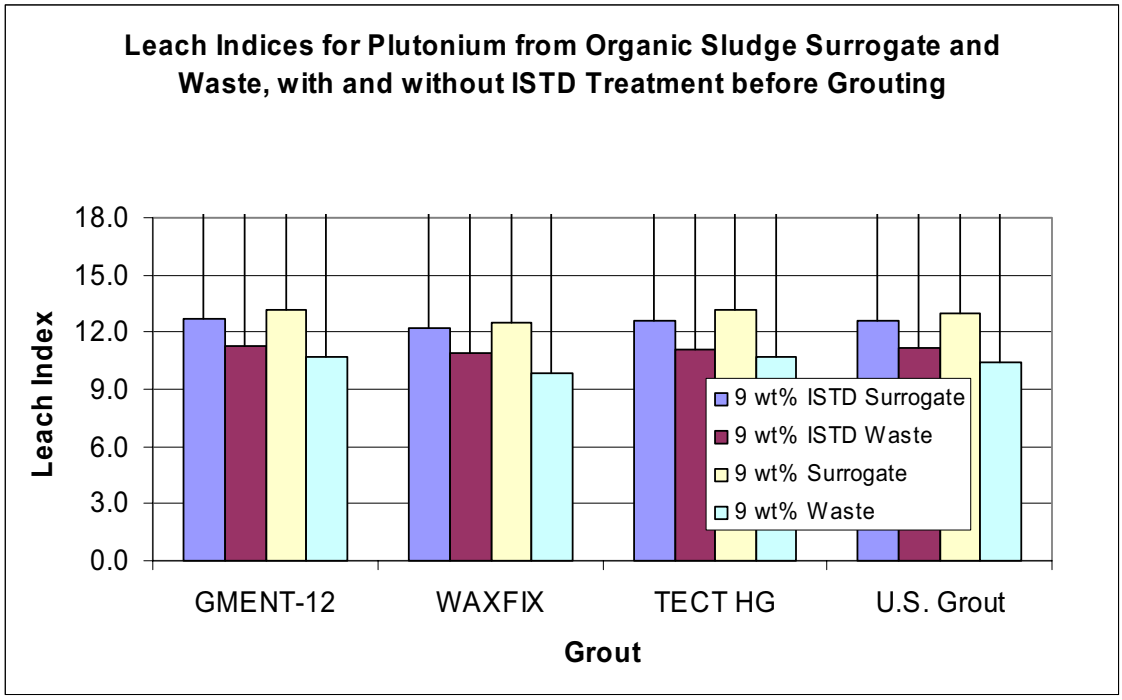

Figure 67. Leach indices for plutonium for organic sludge surrogate and waste, with and without ISTD treatment at 450°C (842°F) before grouting.

Less than 2/3 of the measured values in Figure 67 were below detection limits for the analytical equipment. Values shown are calculated based on the instrument detection limit. The error bars are used to show that the true value is equal to or greater than the calculated value based on the detection limit.

5.2.5 In Situ Grouting Contaminant Transport Summary

The waste loadings used in the leach tests were determined by the maximum amount of waste or surrogate that could be added to the grout and still maintain a cohesive sample. The leach index was expected to decrease as waste loading increased, this was not observed. For many of the samples containing TRU isotopes (i.e., uranium, americium, plutonium, and neptunium), the concentrations of radionuclides in the leachate were below the detection limit so that the leach index was calculated from the detection limit. For the samples containing TRU isotopes, most (with the exception of neptunium) of the leach indices are greater than 10, indicating low effective diffusivity and high resistance to leaching. The grouts tested here all performed similarly well. Because most data came back nondetectable, the leach indices did not vary much either. Radionuclides were added at concentrations that were detectable in the untreated waste; therefore, all of the grouts were successful at reducing the leachability of the radionuclides tested. The leach index values for all the radionuclides (TRU and non-TRU) were approximately the same in WAXFIX. This is not surprising since WAXFIX works by encapsulation of the contaminant. For all of the samples containing non-TRU isotopes (i.e., carbon, technetium, and iodine), concentrations of the radionuclides in the leachate were above detection limits. The leach index of non-TRU isotopes was generally lower than that for TRU isotopes in U.S. Grout and TECT HG. Cementitious grouts immobilize contaminants by a combination of chemical interaction and

encapsulation. The difference seen between the two classes of radionuclides with the cementitious grouts is probably caused by a difference in the chemical interactions between the radionuclides and the grouts.

The addition of waste materials generally decreased the compressive strength and increased the hydraulic conductivity and porosity of the grouts compared to neat grout samples. These measurements suggest that the ability of grouts to immobilize contaminants decreased with the presence of waste. Based on results of ANS leach tests conducted on grouted samples, there is no clear best choice among formulations of grouts tested for all types of waste and contaminants. In accordance with the ANS procedure, grouted samples are compared on the basis of the calculated leach index with a 99.9% confidence range. WAXFIX did not have the compressive strength of cementitious formulations and was less effective at immobilizing TRU contaminated organic and inorganic sludge surrogates than the three cementitious grout formulations tested, suggesting that Portland-cement-based grouts should be a better choice for jet grouting TRU contaminants in the SDA. For jet grouting of non-TRU contaminants based on the leach index, Portland cement with slag, Portland cement with slag and thiosulfate, WAXFIX, and GMENT-12 would be the best and essentially equal choices for immobilization of C-14, Tc-99, and I-129 in soil. If cost also is considered, then the Portland cement with slag likely will be the best choice if a well-characterized and consistent source of slag is available.

In an effort to put the leach results presented in this report with work done previously, data from this report were compared to the leach values presented in the *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (Holdren and Broomfield 2004). Holdren and Broomfield (2004) identify values for diffusion coefficients for contaminants from cement-based grouts (see Table 3). These values, which were calculated and recommended by Pacific Northwest National Laboratory (PNNL), represent the assumptions to be used for modeling the long-term effectiveness of the in situ grouting alternative (Holdren and Broomfield 2004, Riley and Lo Presti 2004).

Table 3. Cement-based grout diffusion coefficients (cm^2/s).[a]

Contaminant	PERA[b]	Feasibility Study[c]
Ac-227	1.00E-15	5.00E-08
Am-241	1.00E-15	7.14E-13
Am-243	1.00E-15	7.14E-13
C-14	1.00E-14	2.48E-13
I-129	1.00E-10	9.03E-09
Nb-94	1.00E-10	5.00E-08
Np-237	1.00E-15	1.00E-11
Pu-238	1.00E-15	1.86E-11
Pu-239	1.00E-15	1.86E-11
Pu-240	1.00E-15	1.86E-11
Tc-99	1.00E-12	3.87E-09
U-233	1.00E-15	1.50E-11
U-234	1.00E-15	1.50E-11
U-235	1.00E-15	1.50E-11

Table 3. (continued).

Contaminant	PERA[b]	Feasibility Study[c]
U-236	1.00E-15	1.50E-11
U-238	1.00E-15	1.50E-11

a. This table is edited from Table A-1 in Holdren and Broomfield (2004).
b. Zitnik et al. 2002.
c. Green shading indicates a change compared to the value used in the PERA (Zitnik et al. 2002), based on Riley and Lo Presti (2004).

PERA = *Preliminary Evaluation of Remedial Alternatives*.

The diffusion coefficient values presented in Table 3 are based on the mean effective diffusivities from a set of ANSI 16.1 leach test data assembled from the literature (Riley and Lo Presti 2004). The data presented in this report were obtained using the same basic procedure (i.e., ANSI 16.1) that was used for the data in the PNNL report (Riley and Lo Presti 2004). The analytical techniques used for the data in this report are consistent with the range of analytical techniques used to generate the data in the PNNL report. The data in this report are presented and compared as leach index values per ANSI 16.1. To compare the data from this report to the values in the PNNL report, the PNNL data was converted to leach index values. Table 4 shows the minimum and maximum leach index values for the PNNL data and the data for grout and soil from this report. A quick review of some of the literature referenced (Akers, Kraft, and Mandler 1994a; Akers, Kraft, and Mandler 1994b; Serne, Martin, and Legore 1995; and Serne et al. 1989) in the PNNL report indicated that most of the data used to develop the numbers presented in the PNNL report were from samples made from cementitous grouts and soil-like materials. Therefore, the samples from this report used for comparison are those made from cementitous grouts and soil. Comparison of the minimum and maximum values for the leach index from the PNNL report and this report show that the two sets of data generally match very well. Many of the data reported in this report are based on nondetect analytical results. In these cases, the leach index was calculated based on the detection limit. The value stated for the leach index represents the minimum value of the leach index for that sample.

Table 4. Minimum and maximum leach index values, based on standard deviations, for contaminants in grouted waste: comparison of data presented in the Pacific Northwest National Laboratory report (Riley and Lo Presti 2004) to data presented in this report.

Source	Contaminant of Concern	Grout/Waste Matrix	Minimum	Maximum	N[(a)]
PNNL report	Americium-241	Cementitious/Unknown[d]	11.1[e]	15.2[e]	3
PNNL report	Americium-243	Cementitious/Unknown[d]	11.1[e]	15.2[e]	3
This report	Americium	GMENT/Soil	11.2	[c]	3
This report	Americium	U.S. Grout/Soil	11.3	[c]	3
This report	Americium	TECT HG/Soil	11.2	[c]	3
PNNL report	Carbon-14	Cementitious/Unknown[d]	12.0[e]	14.2[e]	6
This report	Carbon-14	Saltstone/Soil	9.4	11.4	3
This report	Carbon-14	GMENT/Soil	15.8	15.8	3
This report	Carbon-14	U.S. Grout/Soil	6.4	7.8	3
This report	Carbon-14	TECT HG/Soil	7.2	7.8	3
This report	Carbon-14	C/Soil	10.8	14.2	3
This report	Carbon-14	CS/Soil	15.5	18.5	3

Table 4. (continued).

Source	Contaminant of Concern	Grout/Waste Matrix	Minimum	Maximum	N[(a)]
This report	Carbon-14	CST/Soil	16.8	18.6	3
This report	Carbon-14	CF/Soil	11.2	11.4	3
This report	Carbon-14	CFT/Soil	11.0	12.0	3
PNNL report	Iodine-129	Cementitious/Unknown[d]	7.4[e]	10.9[e]	10
This report	Iodine[b]	Saltstone/Soil	7.2	7.4	3
This report	Iodine[b]	GMENT/Soil	8.3	8.5	3
This report	Iodine[b]	U.S. Grout/Soil	7.2	7.4	3
This report	Iodine[b]	TECT HG/Soil	6.3	10.7	3
This report	Iodine[b]	C/Soil	10.1	10.3	3
This report	Iodine[b]	CS/Soil	7.5	8.3	3
This report	Iodine[b]	CST/Soil	7.9	10.3	3
This report	Iodine[b]	CF/Soil	7.5	10.0	3
This report	Iodine[b]	CFT/Soil	9.9	10.1	3
PNNL report	Neptunium-237	Cementitious/Unknown[d]	7.3[e]	13.3[e]	0
This report	Neptunium	GMENT/Soil	14.6	c	3
This report	Neptunium	U.S. Grout/Soil	14.8	c	3
This report	Neptunium	TECT HG/Soil	14.5	c	3
PNNL report	Niobium-94	Cementitious/Unknown[d]	6.0[e]	10.0[e]	0
This report	Niobium	N/A	Not measured	Not measured	--
PNNL report	Plutonium-238	Cementitious/Unknown[d]	9.9[e]	16.0[e]	7
PNNL report	Plutonium-239	Cementitious/Unknown[d]	9.9[e]	16.0[e]	7
PNNL report	Plutonium-240	Cementitious/Unknown[d]	9.9[e]	16.0[e]	7
This report	Plutonium	GMENT/Soil	11.0	c	3
This report	Plutonium	U.S. Grout /Soil	11.1	c	3
This report	Plutonium	TECT HG /Soil	11.0	c	3
PNNL report	Technetium-99	Cementitious/Unknown[d]	7.4[e]	11.7[e]	43
This report	Technetium-99	Saltstone/Soil	9.7	10.1	3
This report	Technetium-99	GMENT/Soil	10.0	10.8	3
This report	Technetium-99	U.S. Grout/Soil	7.0	7.0	3
This report	Technetium-99	TECT HG/Soil	7.0	7.8	3
This report	Technetium-99	C/Soil	9.6	10.6	3
This report	Technetium-99	CS/Soil	10.9	12.9	3

Table 4. (continued).

Source	Contaminant of Concern	Grout/Waste Matrix	Minimum	Maximum	N[(a)]
This report	Technetium-99	CST/Soil	12.4	13.6	3
This report	Technetium-99	CF/Soil	9.8	10.0	3
This report	Technetium-99	CFT/Soil	9.5	10.5	3
PNNL report	Uranium-233	Cementitious/Unknown[d]	10.3[e]	12.4[e]	5
PNNL report	Uranium-234	Cementitious/Unknown[d]	10.3[e]	12.4[e]	5
PNNL report	Uranium-235	Cementitious/Unknown[d]	10.3[e]	12.4[e]	5
PNNL report	Uranium-236	Cementitious/Unknown[d]	10.3[e]	12.4[e]	5
PNNL report	Uranium-238	Cementitious/Unknown[d]	10.3[e]	12.4[e]	5
This report	Uranium	GMENT/Soil	11.9	c	3
This report	Uranium	U.S. Grout /Soil	11.9	c	3
This report	Uranium	TECT HG /Soil	11.8	c	3

a. Number of data points.
b. Iodine-129 and iodine-127 were used.
c. Greater than two-thirds of the analyses for this test were nondetectable. The detection limit was used to calculate the leach index. The mean leach index represents the minimum leach index for those samples.
d. A quick review of some of the literature referenced in the PNNL report (Akers, Kraft, and Mandler 1994a; Akers, Kraft, and Mandler 1994b; Serne, Martin, and Legore 1995; and Serne et al. 1989) indicated that most of the data used to develop the numbers presented in the PNNL report were from samples made from cementitous grouts and soil-like materials. Therefore, the samples from this report that are used for comparison are made from cementitous grouts and soil.
e. The PNNL leach index (L) values presented in this table were calculated from the minimum and maximum effective diffusivity (D) values presented in the PNNL report by the relationship L = log (1/D).

C = Portland cement
CS = Portland cement and slag
CST = Portland cement, slag, and thiosulfate
CF = Portland cement and fly ash
CFT = Portland cement, fly ash, and thiosulfate
PNNL = Pacific Northwest National Laboratory

5.3 Evaluate WAXFIX for Use as a Grout

Tests used nonradioactive and radioactive surrogates and waste as noted in the text.

5.3.1 Hydrogen Generation

A special test was designed to determine the rate of radiolytic generation of hydrogen gas in WAXFIX. Because of difficulty in gaining approval to work with Pu-238, another isotope was selected for use in the hydrogen-generation test. Uranium-233 was selected as the radiation source because of its high rate of decay and its availability at the INL Site in a usable form. Details of test protocol, equipment, and results are provided in Appendix F. Gas chromatography was used to measure hydrogen generated during the test. Blank generator systems subjected to the same analyses as the test systems showed no hydrogen present throughout the test period. For U-233 systems, the hydrogen production rate fell within the expected region for the radioactive source in the presence of paraffin-based WAXFIX. These levels should not pose a problem in the SDA under a properly constructed cap. Table 5 summarizes results of the hydrogen-generation tests.

Table 5. Mass-normalized and volume-adjusted net hydrogen-generation rates.

Generator	Mass Uranium Oxide (g)	Accumulated Average Hydrogen-Generation Rate (mol/[g of uranium oxide/minute])	Standard Deviation	Differential Average Hydrogen-Generation Rate (mol/[g of uranium oxide/minute])	Standard Deviation
U1	0.163	2.57E-10	7.04E-11	1.77E-10	1.06E-10
U2	0.078	6.72E-11	1.74E-11	3.96E-11	1.31E-11
U3	0.016	2.07E-10	8.71E-11	1.55E-10	1.18E-10
U4	0.006	2.51E-10	9.46E-11	2.00E-10	1.34E-10
B1	0	0	N/A	0	N/A
B2	0	0	N/A	0	N/A

5.3.2 Boron Retention

The possibility of injecting WAXFIX into a waste zone where plutonium and uranium could be present raised the question of criticality. Two tests determined the degree of boron separation that might result if boronated WAXFIX were injected into an SDA waste zone. The boron—sodium borate dissolved in glycerin—was in a particulate form. The objective of the first test was to determine whether boron would settle in hot paraffin, developing a boron concentration gradient. The purpose of the second test was to investigate whether boron would be filtered from molten paraffin as the paraffin passed through soil. Details of the test procedures and results are in Appendix E.

Sentieri (2003) stated that the presence of paraffin grout within the SDA would not lead to formation of a critical mass. At this point, testing had begun using density changes in the WAXFIX to determine loss of boron. Preliminary results indicated that the boron settled in the molten paraffin and that the boron was filtered from the paraffin as the paraffin passed through the soil matrix. The next step would have been a chemical analysis to validate the method of using density change to determine boron loss; however, because of Sentieri's finding, boron testing was halted.

5.3.3 U.S. Department of Transportation Oxidizer

U.S. Department of Transportation oxidizer tests (Yancey et al. 2003, Section 4.3.3.2) were included in the preremedial design studies to evaluate whether the presence of WAXFIX increases the potential for nitrate salts (the primary ingredient of the Pad A nitrate salts) to act as an oxidizer. Because the possibility for a rapid reaction is present if nitrates are involved in an accidental fire during storage or shipping, the objective of these tests was to determine whether sodium nitrate encapsulated in paraffin (WAXFIX) would be classified as a U.S. Department of Transportation oxidizer. The oxidizer tests were ". . .designed to measure the potential for a solid substance to increase the burning intensity of a combustible substance when the two are thoroughly mixed. . ." (Milian et al. 1997).

Project personnel decided that because the base material of WAXFIX is paraffin, WAXFIX should react similarly with an oxidizer. Research into previous tests with paraffin revealed data showing that paraffin retards the oxidizing potential of nitrate salts. These data were taken as sufficient to demonstrate the potential effect of WAXFIX coming into contact with SDA nitrate salts without additional testing.

Appendix F describes in more detail the U.S. Department of Transportation oxidizer testing found in the literature.

5.3.4 WAXFIX Conclusions

While WAXFIX consistently had the lowest hydraulic conductivity and porosity values, WAXFIX did not show the highest leach indices for contaminants when compared to cementitious grouts. The diffusivity for WAXFIX was generally independent of the contaminant. This suggests that a physical rather than chemical process controls immobilization of contaminants in WAXFIX. The connected water-accessible porosity of cementitious grouts is higher than that of WAXFIX, but this does not necessarily translate to a higher leach index for individual contaminants. Cementitious grouts have the capacity to chemically interact (adsorption and complexation) with some of the contaminants of interest, thereby increasing the leach index of the contaminant. The data for TRU contaminants (uranium, plutonium, neptunium, and americium) suggest that the grout chemically interacted with the contaminants, thereby reducing the leachability of the contaminants below that seen in WAXFIX. The leachability of the non-TRU contaminants was higher in the cementitious grouts than in WAXFIX, suggesting that chemical interactions between the grout and the contaminants did not act to reduce mobility.

WAXFIX does not appear to have any problems associated with acting as a moderator for criticality (Sentieri 2003). Hydrogen generation should also not be a factor for concern when grouting the SDA. However, higher loadings of the tested waste and surrogate generally are not tolerated. As expected, WAXFIX generally had the lowest compressive strength for the grouts tested. This should not be a concern when creating a large area monolith, as the lower compressive strength is not a critical factor. It would be more critical if individual columns were desired to help support an engineered cap. Loomis et al. (2003) found that WAXFIX was able to permeate through the voids of waste being grouted. WAXFIX was successfully used on the beryllium blocks in the SDA.

6. DATA ANALYSIS AND INTERPRETATION—EX SITU GROUTING

Tests in this section used Pad A waste containing radionuclides, chromium, and nitrate salts, as described. One of the potential uses of ESG is reducing mobility of contaminants of interest. Grouts can reduce contaminant mobility by macroencapsulation, chemical interaction, or a combination of the two processes. For grouts used in this study, WAXFIX and Polysiloxane reduce mobility primarily by macroencapsulation, and Saltstone reduces mobility through a combination of chemical interaction and macroencapsulation. The contaminants studied for these tests were uranium, chromium, and nitrate.

The mobility of chromium was measured using the toxic characteristic leaching protocol. In each waste form and at all loading levels, chromium leached less than the toxicity characteristic level of 5.0 mg/L (EPA 268_40). The universal treatment standard has a more conservative treatment level of 0.60 mg/L (EPA 268_48) than the toxicity characteristic leaching procedure test. Using the universal treatment standard, only the control (0 wt%) and the 25 and 50 wt% samples of Saltstone passed the universal treatment standard of 0.60 mg/L (EPA 268_48). Figure 68 summarizes the results. Note that Saltstone leach levels for the 25 and 50 wt% samples were less than the control sample. This may be because of the bleed-water problem (see Appendix Q for details) in that the chromium left the sample in the bleed water and was not present in the final grout subjected to toxic characteristic leaching protocol. Bleed water formed on and around the Saltstone samples during the curing process. The bleed water contained measurable quantities of contaminants of interest. This contaminated bleed water was, in part, responsible for depleting or reducing the concentration of some of the contaminants being tested. In testing the bleed-water samples, chromium was found at 220 mg/L, which represents 16.8 wt% of chromium in the 25 wt% sample. For the 50 wt% sample, chromium was found at 577 mg/L in the bleed

water, which is 7.7 wt% of chromium in the sample. Thus, a portion of the chromium is in the bleed water, but the majority is retained in grout. This also would be a concern in the field where it would not be desirable for bleed water containing high concentrations of the contaminant of concern to migrate away from the grouted area during the curing process. This likely can be corrected by changing the ratios of water-to-grout in the final grout before implementation.

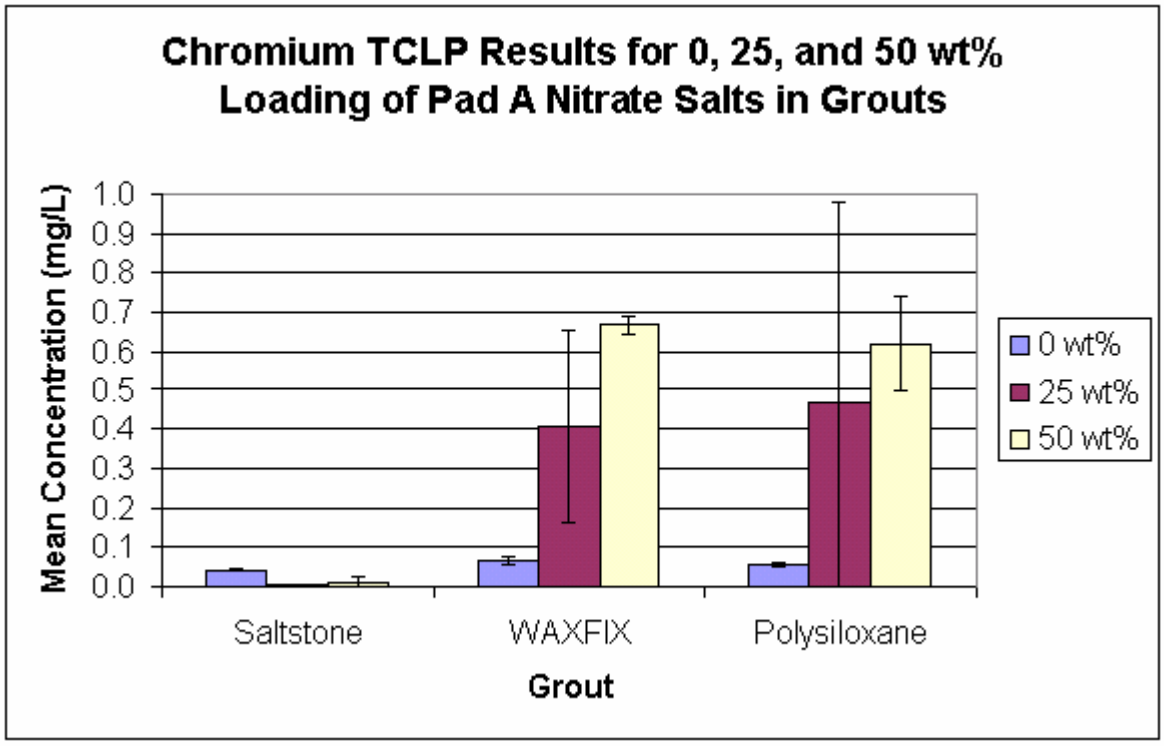

Figure 68. Toxic characteristic leaching protocol results for chromium.

The mobility of selected radionuclide contaminants was measured using the abbreviated ANS leaching protocol. These tests were performed according to the ANS leach test. These tests were specified in Section 4.3.3.9 of Yancey et al. (2003). The abbreviated protocol was selected to decrease the overall length of the studies (1 week instead of 3 months).

The 5 × 10-cm (2 × 4-in.) cylindrical samples specified in ANS 16.1 were substituted with 2 × 3-cm (0.75 × 1.2-in.) samples to decrease radiological control concerns. The calculations for leach indices account for sample dimensions, so that the results reported here are comparable to those that would have been measured for 2 × 4-in. samples. A 99.9% confidence interval is applied to the value to ensure a conservative approach in terms of seeing differences among waste forms.

Leach indices for uranium from Pad A waste are presented in Table 5. The leach index is the log of the inverse of the diffusivity. Therefore, a higher leach index should translate to a lower likelihood for waste leaching, and, conversely, a lower leach index translates to a greater likelihood for leaching. The data indicate that more of the uranium leached from the WAXFIX and the Polysiloxane samples than from the Saltstone samples. All of the leach indices were greater than 8 as noted in Table 6. This simply means that the grouts were retarding the leachability for the COCs tested. Only the overall leach index is used to judge the quality of the waste form; however, the individual indices give an indication when the uranium leached.

Table 6. American Nuclear Society leach index results for uranium.

Grout	Waste Loading (wt%)	Uranium Leach Index	99.9% Confidence Interval
Saltstone[a]	25	16.3	0.8
Saltstone[a]	50	15.8	1.9
WAXFIX	25	8.9	0.4
WAXFIX	50	8.6	0.4
Polysiloxane	25	9.3	1.2
Polysiloxane	50	8.9	1.3

a. Values for Saltstone are suspect because of bleed water.

Since the Saltstone samples showed so little uranium leaching, the bleed water was suspected. In the bleed water, a total of 0.12 mg of uranium was found for the 25 wt% sample and 0.1 mg for the 50 wt% sample. These represent 2.3 and 1.4 wt% of the total uranium in the 25 and 50 wt% samples, respectively. Thus, the majority of uranium seems to be retained in the grout-waste form.

The Saltstone, WAXFIX, and Polysiloxane show similar nitrate leach results over time. Saltstone shows an extremely high leach rate at first and then slows to almost nothing at later times, suggesting that most of the nitrate leaches immediately, and none is left to leach in later intervals. This again indicates that the Saltstone formulation is unstable as a waste form. The very high nitrate concentration in this formulation may be the problem. The mean overall leach indices for nitrate are shown in Table 7 (additional detail is presented in Appendix Q). Except for 25 wt% loading of Saltstone, no significant difference was observed between the grouts and waste loadings.

Table 7. Calculated leach indices for nitrate.

Grout	Waste Loading (wt%)	Leach Index	99.9% Confidence Interval
Saltstone	25	6.9	0.2
	50	8.0	4.3
WAXFIX	25	8.1	0.2
	50	8.0	0.1
Polysiloxane	25	8.7	1.2
	50	8.2	1.0

7. QUALITY ASSURANCE AND QUALITY CONTROL

All samples were prepared and tested in triplicate except where noted.

For the leach indices, statistics were calculated at a two-tailed 99.9% confidence level using the Student's *t* test as specified in the ANS procedure. Statistics for all other measurements were calculated at

a two-tailed 95% confidence level using the Student's *t* test. The 95% confidence level was selected since the population size, three replicates, was small and the systems being measured contained many variables.

Detection limits were established where appropriate. When a sample was below detection for the measurement of interest, the value was recorded as less than the detection limit. For the purposes of calculation, the detection limit was used for those measurements with values less than the detection limit. In all cases, this approach was conservative in terms of overall performance of the material being evaluated. Using the detection limit for the value ensured that performance of the material was not overstated.

All instrumentation was in calibration, and appropriate standards and calibration curves were used where appropriate.

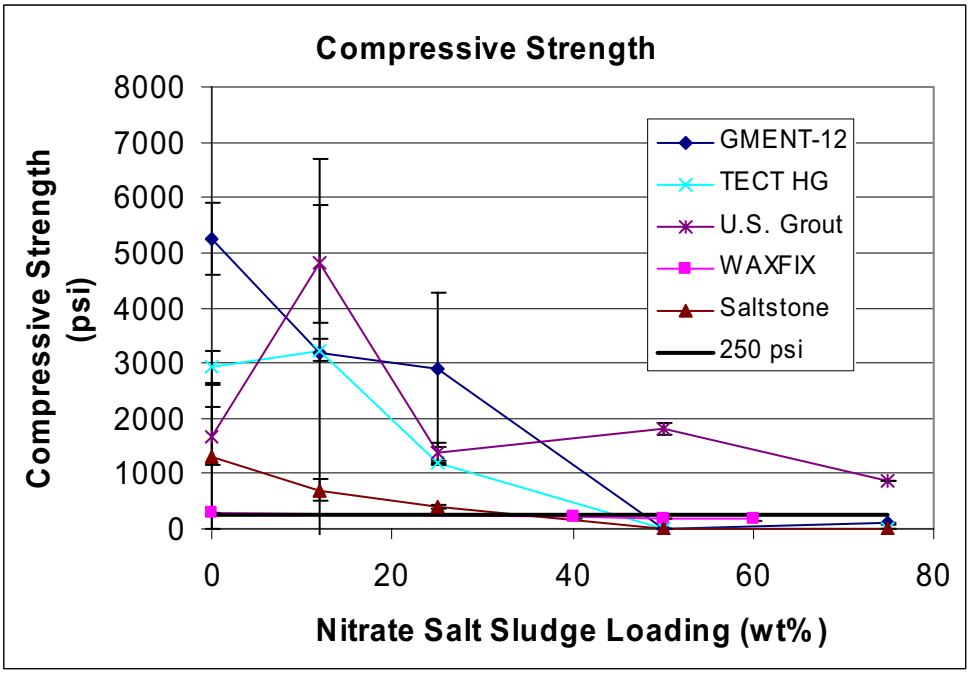

Figure 69. Compressive strength with nitrate salt sludge as a surrogate.

Data were handled at Quality Level 3, which means chain-of-custody forms were not used, but all samples were given unique sample identification numbers.

8. CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations are organized along the three major technology applications explored by testing: ISTD, ISG, and ESG.

8.1 Conclusions

8.1.1 In Situ Thermal Desorption

Based on current and previous testing for ISTD, nitrate salts are expected to react exothermically with various forms of carbon in the waste. As shown most clearly in TGA tests, the chemical form of

carbon and rate of temperature increase of the system affect the magnitude and intensity of the reaction. The drum-scale reactivity experiments failed to demonstrate a method to heat nitrate salt surrogate and carbon-containing materials in a manner that maintained control over the reaction between nitrate and carbon. Based on TGA and drum-scale results, it may be possible to heat mixtures of nitrate and carbon-containing waste in a manner that keeps the reaction under control, but it would require slow rates of heating and control of hot-spot formation.

In situ thermal desorption should be able to remove VOCs and oils from the subsurface through a combination of volatilization, oxidation, and reduction. The fate of radionuclides during ISTD cannot be conclusively stated based on data collected during this testing.

Elimination of organic compounds and the nitrates would simplify and improve the overall performance of grout in the waste; however, all of the grouts tested can tolerate some amount of organic and nitrate compounds. Elimination of only the VOCs would significantly reduce the inventory of chlorinated organic compounds, some of which are COCs, and would reduce by about half the total mass of organic compounds present in the waste. Volatile organic compounds could probably be removed at temperatures below 230°C (584.2°F) to avoid the nitrate-cellulose reaction, but additional testing and modeling would be required to demonstrate the technical implementability and economic feasibility of this approach. Using ISTD to reduce the total mass of VOCs in the waste seam will cause grouting to be more effective by increasing the void volume within the waste that is accessible to grout, thus decreasing the ratio of waste-to-grout, and by improving the quality of grout placed in areas that contain VOCs. (Grouts only tolerate limited amounts of VOCs, so removing VOCs would improve the quality of grout in those regions.)

Although there are benefits that can be derived from the ISTD process, it is recommended that ISTD be ruled out as a treatment option at the SDA because of the potential concerns of maintaining control of the reaction, especially in the areas containing nitrates and carbon-containing material, and because there are also conditions where there may be a potential for ISTD to actually increase the mobility of some of the COCs.

8.1.2 In Situ Grouting

Waste containers used in the SDA include carbon steel drums, stainless steel drums, and cardboard and wood boxes. Based on recent excavations in Pit 9, most of the carbon steel drums that contain waste are badly corroded (DOE-ID 2004). Drums in Pit 9 were randomly dumped and stacked; these drums were compacted once in place by rolling heavy equipment over them. Many of the drums were crushed by the heavy equipment.

If integrity of drums is already compromised, such as is expected for carbon steel drums and nonmetal containers, then jet grouting is recommended. Jet grouting will mix grout and waste and reduce mobility of contaminants by lowering hydraulic conductivity of the waste zone and encapsulating contaminants. In this situation, cementitious grouts would generally be preferred over WAXFIX for jet grouting because of their higher density, which promotes mixing, and lower cost. The preferred cementitious grout formulation depends on the type of waste to be grouted.

Compressive strength, porosity, and hydraulic conductivity are important parameters to consider when evaluating immobilization potential of a grout for a specific contaminant, but none of them are direct indicators of leach resistance. If grout functions only as a macroencapsulation agent, then chemistry of the radionuclide is not important. The radionuclide and the type of waste matrix are factors to consider when choosing the type of grout for stabilization. If grout immobilizes contaminants through a combination of chemical interaction and macroencapsulation, then chemistry of the contaminant is

important. Transuranic radionuclides may behave differently from non-TRU radionuclides, with respect to leaching, when grouted in cementitious materials. When grouted with WAXFIX, a paraffin-based material, there was no difference in leaching among radionuclides tested.

WAXFIX generally produces samples with the lowest hydraulic conductivity and porosity; however, this does not necessarily equate to a reduction in radionuclide release. As mentioned earlier, a grout that functions by macroencapsulation alone will work equally well or badly regardless of the contaminant. A grout that functions by macroencapsulation and chemistry may work well with some contaminants but may not work as well for other contaminants. The pH and oxidation-reduction potential of the leaching solutions can provide some insight into this question (see Appendix N for details on pH and oxidation-reduction potential values). The pH of WAXFIX samples is almost always lower than that of cementitious samples. The oxidation-reduction potential of WAXFIX samples is usually higher than the other grouts, indicating that the samples remain more oxidized than in cementitious grouts. The combination of having a lower pH and higher oxidation-reduction potential generally does not favor immobilization of radionuclide contaminants, but this is not necessarily important for WAXFIX since the primary mechanism of WAXFIX immobilization is physical encapsulation rather than chemical interaction.

All of the grout formulations (GMENT-12, U.S. Grout, TECT HG, WAXFIX, Portland cement, and Portland cement with slag) performed well relative to their compressive strength up to a soil loading of 50 wt%. The WAXFIX achieved its highest compressive strength at 70 wt%. At 75 wt%, most of the cementitious grouts failed to make a cohesive sample. Based on compressive-strength measurements on samples mixed with 50 wt% soil, the Portland cement, Portland cement with blast furnace slag, and GMENT-12 grout had the highest compressive strength. If cost were incorporated into the decision, then the Portland cement and Portland cement with slag grout would be the grout of choice. WAXFIX has an advantage when mixed with soil at 70 wt% loading. The cementitious grout at this loading does not form a cohesive sample.

When grouts were mixed with organic sludge surrogate, both current tests with WAXFIX and previous tests (Loomis et al. 2003) showed that only the cementitious grouts could take 9–10 wt% waste and still meet the 250-psi loading. GMENT-12 had the greatest compressive strength up to 9 wt% organic sludge.

When nitrate salts were mixed with grout, WAXFIX and U.S. Grout were able to maintain a cohesive sample up to a 60 wt% nitrate salt loading, other cementitious grouts were able to handle a 12 wt% waste loading, and some grouts could maintain a cohesive sample as high as 25 wt%. This suggests that WAXFIX or U.S. Grout may be the appropriate choice for regions containing a high percentage of nitrate salt material.

By thermally treating (ISTD) organic sludge before grouting, the cementitious grouts were able to produce samples with acceptable compressive strength up to a waste loading of 30 wt%. WAXFIX samples were able to handle a 60 wt% loading and still maintain an acceptable compressive strength. GMENT-12 grout had the highest compressive strength for ISTD-treated organic sludge.

The hydraulic conductivity and porosity of WAXFIX, TECT HG, GMENT-12, U.S. Grout, and grout formulations of Portland cement and Portland cement with slag were tested without any surrogate or waste added. These tests showed that WAXFIX had significantly lower porosity and hydraulic conductivity than any of the cementitious grouts. The GMENT-12, TECT HG, Portland cement, and Portland cement with slag formulations had lower hydraulic conductivity and porosity than U.S. Grout. Soil was added to the same grout formulations, and the hydraulic conductivity and porosity tests were repeated at a soil loading of 50 wt% for the cementitious formulations and at a soil loading of 70 wt% for

WAXFIX. Porosity of WAXFIX with soil samples was again significantly lower than for the other grouts, while porosity of U.S. Grout with soil samples was higher than for other grout formulations. No difference was observed among any of the grout formulations with respect to hydraulic conductivity. This suggests that U.S. Grout may not be the best grout formulation when water transport is a key issue. If water transport is the most important factor, the WAXFIX samples had the lowest porosity and hydraulic conductivity measured. Combining these data with the compressive strength data shows that GMENT-12 has the highest compressive strength and has the lowest porosity for the cementitious grouts, and would be the best choice based on both water transport and strength for grout and soil mixtures if compressive strength is a significant factor in choosing grout.

Hydraulic conductivity was measured of WAXFIX, TECT HG, U.S. Grout, and GMENT-12 grout formulations with organic sludge surrogate. The grouts were mixed with organic sludge surrogate at a loading of 9-10 wt%. WAXFIX samples had significantly lower hydraulic conductivity than the other grouts. No difference was observed between GMENT-12 and TECT HG samples, and U.S. Grout had the highest hydraulic conductivity. Based on hydraulic conductivity, WAXFIX would be the grout of choice. By considering both hydraulic conductivity and compressive strength, then GMENT-12 grout stands out as best. This is because WAXFIX was unable to maintain compressive strength greater than 250 psi, and while TECT HG and GMENT-12 performed equally well for hydraulic conductivity; GMENT-12 had a higher compressive strength value than TECT HG when mixed with organic sludge surrogate.

WAXFIX was mixed with nitrate salts at a loading of 60 wt%, while cementitious grouts were tested at 12 wt% (Saltstone was tested at 25 and 50 wt% in the ex situ grouting tests). There was no difference among WAXFIX, TECT HG, and U.S. Grout, but GMENT-12 was significantly higher (95% confidence interval). While hydraulic conductivity of WAXFIX was not significantly different than TECT HG and U.S. Grout, note that WAXFIX had five times more nitrate salt surrogate mixed with it than other grouts. In this case, the WAXFIX grout would be a good choice. At 60 wt% nitrate salt, the compressive strength also was good for WAXFIX and nitrate salt sludge. In the case of Pad A waste, it is expected that the waste will be removed, grouted, and placed in a pit at the SDA. In this case, based on current results, grouting with WAXFIX would be the best choice. Saltstone, a Portland-cement-based grout, was also tested, and, based on the results, might work effectively with some modification of the recipe used in this report.

The ISTD-treated organic sludge surrogate was mixed with each grout at 30 wt% for cementitious grouts and 60 wt% for WAXFIX. Hydraulic conductivity was significantly lower for WAXFIX than cementitious grouts. No difference was observed among cementitious grouts. This suggests that when strength is not as important as water transport, WAXFIX is a better choice than cementitious grout formulations tested.

GMENT-12, U.S. Grout, and TECT HG grout formulations were mixed with organic sludge surrogate, organic sludge waste, inorganic sludge surrogate, soil, or nitrate salt waste. No significant difference (99.9% confidence interval) was observed among grout formulations or waste and surrogates in terms of their abilities to immobilize americium, uranium, neptunium, and plutonium as indicated by the leach index. The leach index for neptunium from WAXFIX with 30 or 60 wt% inorganic surrogate or 30 wt% soil was significantly lower than with the cementitious grout formulations. The leach index for uranium from WAXFIX with 30 wt% soil was also significantly lower than with the cementitious grout formulations. This highlights the complexities of selecting grouting materials. Based on leaching tests, WAXFIX is the least effective of the grouts tested for immobilizing TRU contaminants, despite having a lower hydraulic conductivity and porosity than other grouts tested. Combining leaching, hydraulic conductivity, porosity, and compressive-strength data suggests that GMENT-12 or TECT HG is the best choice for grouting TRU contaminants in the SDA. When this is compared with hydraulic conductivity, porosity, and compressive strength, GMENT-12 grout stands out as the best overall grout tested.

Soil was spiked with non-TRU contaminants, C-14, I-129, and Tc-99 and mixed at 30 wt% with U.S. Grout, TECT HG, GMENT-12, and WAXFIX; the spiked soil also was mixed at 50 wt% with Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and sodium thiosulfate, or Portland cement with slag and sodium thiosulfate. For C-14, the highest leach index values were shown by WAXFIX, GMENT-12, Portland cement with slag, and Portland cement with slag and thiosulfate. For iodine, in the nonproprietary grout formulations (see Figure 54), Portland cement and Portland cement with fly ash and thiosulfate were higher than Portland cement with slag and Portland cement with fly ash; WAXFIX was higher than U.S. Grout, Portland cement with slag, and Portland cement with fly ash. For Tc-99, WAXFIX, GMENT-12, Portland cement, Portland cement with slag, Portland cement with slag and thiosulfate, and Portland cement with fly ash and thiosulfate were statistically higher than U.S. Grout. Portland cement, Portland cement with slag and thiosulfate, and Portland cement with fly ash and thiosulfate were also statistically higher than TECT HG.

The U.S. Grout and TECT HG were better at immobilizing the TRU radionuclides than the non-TRU radionuclides. (Portland-cement-fly ash-slag-thiosulfate formulations were not tested with TRU radionuclides.) This is not surprising since the cementitious grouts were originally developed to immobilize TRU contaminants through a combination of encapsulation and chemistry, and the chemistry of TRU and non-TRU contaminants is different. WAXFIX performed equally well for TRU and non-TRU contaminants since WAXFIX functions by physical encapsulation of contaminants. When compressive strength, porosity, and hydraulic conductivity are considered, the best overall grout is GMENT-12.

Among the cementitious grout formulations tested, there was no clear best choice for TRU or non-TRU contaminants. Based on current and previous test results, GMENT-12 and TECT HG are expected to work slightly better for TRU-contaminated waste of the forms tested. Based on current and previous test results, GMENT-12, WAXFIX, or Portland cement with slag, and Portland cement with slag and thiosulfate are expected to perform slightly better for non-TRU contaminants. While WAXFIX has less compressive strength than the other grout formulations tested, it did not perform significantly worse than the other grouts in terms of porosity, hydraulic conductivity, or leachability. If cost also is considered, then the Portland cement with slag is likely to be the best choice if a well-characterized and consistent source of slag is available.

8.1.3 Ex Situ Grouting

Results with the Saltstone grout formulations were surprising. Although Saltstone was originally developed for use with nitrate salt waste, this formulation does not appear to be appropriate for high waste loadings (i.e., greater than 25 wt%) of nitrate salt sludge. Saltstone might work effectively with some modification of the recipe used in this report. As currently formulated, Polysiloxane has a high viscosity, which makes it difficult to mix with the nitrate salt sludge. WAXFIX accepted a high (i.e., 60 wt%) loading of nitrate salt waste, but the potential exists for waste to settle in WAXFIX.

Of the three grout formulations tested, no clear differences appeared in leachability of chrome, nitrate, or uranium among the grout formulations; however, the higher leach indices obtained with Saltstone are suspect because of the presence of bleed water during sample preparation. All of the grout formulations have sufficient compressive strength for use in ESG, but considering leaching, waste loading, and workability, WAXFIX performed the best overall.

8.2 Recommendations

Although there are benefits that can be derived from the ISTD process, it is recommended that ISTD be ruled out as a treatment option at the SDA because of potential concerns of maintaining control

of the reaction, especially in the areas containing nitrates and carbon-containing material, and because there are also conditions in which ISTD could actually increase the mobility of some of the COCs.

Based on the current testing and past studies, the strongest performing grouts, considering physical properties, leaching, and cost, for each class of contaminant and waste are as follows:

- For TRU contaminants in soil, four grouts were evaluated for these contaminants: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In areas where physical support and immobilization of contaminants is needed, GMENT-12 would be preferred, as it performed the best overall.
- For TRU contaminants in organic sludge, four grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In this case, all of the grouts performed equally well at reducing leachability of the TRU contaminants, but GMENT-12 had the highest compressive strength. If organic sludge is to be grouted and if compressive strength is important, then GMENT-12 would be the best choice.
- For TRU contaminants in nitrate salt, five grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, and Saltstone. In areas where carbon steel drums or nonmetal containers were used to contain TRU contaminants in nitrate salt, the integrity of the containers is likely already compromised, and jet grouting could be used to reduce the potential for contaminant transport. Where ISG has been identified for use in nitrate salts, U.S. Grout is recommended because it produces samples with the highest compressive strength and a comparable leach index to the other grouts tested. WAXFIX also produced good leach-resistant samples and could withstand high salt loadings; however, compressive strength was not as good as U.S. Grout.
- For non-TRU contaminants in soil, ten grout formulations were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, Saltstone, Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and thiosulfate, and Portland cement with slag and thiosulfate. Portland cement with slag, Portland cement with slag and thiosulfate, WAXFIX, and GMENT-12 would be the best and essentially equal choices for immobilization of C-14, Tc-99, and I-129 in soil. Based on physical properties, GMENT-12 compared to Portland cement with slag has the same compressive strength and porosity and lower hydraulic conductivity. WAXFIX, compared to GMENT-12 and Portland cement with slag, has a lower compressive strength, lower porosity, and equal hydraulic conductivity. If cost also is considered, then the Portland cement with slag will be the best choice.
- WAXFIX is recommended for ESG of nitrate salt waste. Most Portland cement-based grouts do not tolerate high loadings of salts. Saltstone, a Portland cement-based grout, was tested, and, based on the results, it might work effectively for nitrate salt waste with some modification of the recipe used in this report. WAXFIX, a paraffin-based grout, was able to tolerate high concentrations of salts and maintain a cohesive sample.
- If ISG is used for physical support of a cap, then a cementitious grout would be the preferred choice. Overall, Portland cement with slag, GMENT-12, or U.S. Grout would be the best choices for physical support of the cap. Based on unconfined compressive-strength tests, GMENT-12 was the most tolerant of organic sludge, U.S. Grout was the most tolerant of nitrate salt, and soil was tolerated equally by all three. Since nonproprietary grouts, such as Portland cement with slag, are expected to be less expensive than proprietary grouts, and since volume percentage of organic sludge and nitrate salt waste in the SDA is relatively small, Portland cement with slag is recommended for use as a cap support grout in the SDA.

9. REFERENCES

10 CFR 61, 2005, "Licensing Requirements for Land Disposal of Radioactive Waste," *Code of Federal Regulations*, Office of the Federal Register, January 2005.

42 USC § 9601 et seq., 1980, "Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA/Superfund)," United States Code.

Abbott, David G., 2003, *Feasibility Study Preliminary Documented Safety Analysis for In Situ Thermal Desorption in the Subsurface Disposal Area*, INEEL/EXT-03-00962, Rev. 0, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Adler-Flitton, M. K., C. W. Bishop, M. E. Delwiche, and T. S. Yoder, 2004, *Long-Term Corrosion/Degradation Test Six Year Results*, INEEL/EXT-04-02335, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Akers, D. W., N. C. Kraft, and J. W. Mandler, 1994a, *Release of Radionuclides and Chelating Agents from Cement-Solidified Decontamination Low-Level Radioactive Waste Collected from the Peach-Bottom Atomic Power Station Unit 3,* EGG-2722, Idaho National Engineering Laboratory.

Akers, D. W., N. C. Kraft, and J. W. Mandler, 1994b, *Compression and Immersion Tests and Leaching of Radionuclides, Stable Metals, and Chelating Agents from Cement Solidified Decontamination Waste Collected from Nuclear Power Stations,* NUREG/CR-6201, EGG-2736, Idaho National Engineering Laboratory.

ANS 16.1, 1986, "Measurement of the Leachability of Solidified Low-Level Radioactivity Wastes by a Short-Term Test Procedure," American Nuclear Society.

Arrenholz, D. A. and J. L. Knight, 1991, *A Brief Analysis and Description of Transuranic Wastes in the Subsurface Disposal Area of the Radioactive Waste Management Complex at INEL*, EGG-WTD-9438, Rev. 1, Idaho National Engineering Laboratory.

Becker, B. H., J. D. Burgess, K. J. Holdren, D. K. Jorgensen, S. O. Magnuson, and A. J. Sondrup, 1998, *Interim Risk Assessment and Contaminant Screening for the Waste Area Group 7 Remedial Investigation*, DOE/ID-10569, U.S. Department of Energy Idaho Operations Office.

Blackwood, Larry G. and Cecilia R. Hoffman, 2004, *Validation of the Rocky Flats Plant Radionuclide Inventory in the Historic Data Task Using SWEPP Assay Data*, ICP/EXT-04-00211, Rev. 1, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Clements, Thomas L., Jr., 1982, *Content Code Assessments for INEL Contact-Handled Stored Transuranic Wastes*, WM-F1-82-021, U.S. Department of Energy Idaho Operations Office.

CRC, 2000, *Handbook of Chemistry and Physics*, Boca Raton: Chemical Rubber Company Press.

Dick, John R., 2001, *Nitrate Explosives Tests to Support the Operable Unit 7-13/14 In Situ Vitrification Project*, INEEL/EXT-01-00265, Rev. 0, Idaho National Engineering and Environmental Laboratory.

DOE-ID, 2004, *Remedial Action Report for the OU 7-10 Glovebox Excavator Method Project*, DOE/NE-ID-11155, Rev. 0, U.S. Department of Energy Idaho Operations Office.

DOE-ID, 1991, *Federal Facility Agreement and Consent Order for the Idaho National Engineering Laboratory*, Administrative Docket No. 1088-06-29-120, U.S. Department of Energy Idaho Operations Office; U.S. Environmental Protection Agency, Region 10; and Idaho Department of Health and Welfare.

EPA 268_40, "Treatment Standards for Hazardous Wastes," http://www.epa.gov/epaoswer/hazwaste/ldr/268_40.pdf, Web page visited November 22, 2004, U.S. Environmental Protection Agency.

EPA 268_48, "Universal Treatment Standards," http://www.epa.gov/epaoswer/hazwaste/ldr/268_48.pdf, Web page visited November 22, 2004, U.S. Environmental Protection Agency.

EPA, 1992, *Guide for Conducting Treatability Studies under CERCLA*, EPA/540/R-92/071A, OSWER Directive-9380.3-10, U.S. Environmental Protection Agency.

Hanson, Duane J., Sylvester J. Losinski, Jay T. Brown, and Gretchen E. Matthern, 2005, *Evaluation of Durability of Portland-Cement-Based Grout for Subsurface Applications at OU 7-13/14*, ICP/EXT-05-00789, Rev. 0, Idaho National Laboratory, Idaho Cleanup Project.

Holdren, K. Jean and Barbara J. Broomfield, 2004, *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study*, DOE/ID-11039, U.S. Department of Energy Idaho Operations Office.

Holdren, K. Jean, Bruce H. Becker, Nancy L. Hampton, L. Don Koeppen, Swen O. Magnuson, T. J. Meyer, Gail L. Olson, and A. Jeffrey Sondrup, 2002, *Ancillary Basis for Risk Analysis of the Subsurface Disposal Area,* INEEL/EXT-02-01125, Idaho National Engineering and Environmental Laboratory.

Landman, W. H., Jr., 1981, *Rocky Flats Sludge Composition,* SN TWTF-56, Idaho National Engineering Laboratory.

Liekhaus, K. J., 1991, *Nonradioactive Inventory in Pit 9 at the RWMC*, EDF-ERP-BWP-65, Rev. 2, Idaho National Engineering Laboratory.

Loomis, Guy G. and James O. Low, 1988, *Annual Technology Assessment and Progress Report for the Buried Transuranic Waste Studies Program at the Idaho National Engineering Laboratory (1987)*, EGG-2525, Idaho National Engineering Laboratory.

Loomis, Guy G., Christopher M. Miller, and Stephen W. Prewett, 1997, *Mixed Waste Salt Encapsulation Using Polysiloxane—Final Report*, INEEL/EXT-97-01234, Idaho National Engineering and Environmental Laboratory.

Loomis, Guy G., James J. Jessmore, Jerry R. Weidner, Christopher M. Miller, and Allen L. Sehn, 2003, *Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites*, INEEL/EXT-02-00233, Rev. 1, Idaho National Engineering and Environmental Laboratory.

Low, J. O., D. W. Allman, P. G. Shaw, and C. W. Sill, 1987, *Annual Technology Assessment and Progress Report for the Buried Transuranic Waste Program at the Idaho National Engineering Laboratory*, EGG-2483, Idaho National Engineering Laboratory.

Low, James O., 1985, *Annual Technology Assessment and Progress Report for the Buried Transuranic Waste Program at the Idaho National Engineering Laboratory*, EGG-2429, Idaho National Engineering Laboratory.

McElroy, D. L. and J. M. Hubbell, 1990, *Hydrologic and Physical Properties of Sediments at the Radioactive Waste Management Complex*, EGG-BG-9147, Idaho National Engineering Laboratory.

Milian, L. W., J. H. Heiser, J. W. Adams, and S. P. Rutenkroeger, 1997, *In-Situ Stabilization of TRU/Mixed Waste Project at the INEEL*, BNL-64958, Brookhaven National Laboratory.

Miller, Eric C. and Mark D. Varvel, 2005, *Reconstructing the Past Disposal of Series 743 Waste in the Subsurface Disposal Area for Operable Unit 7-08, Organic Contamination in the Vadose Zone*, INEEL/EXT-01-00034, Rev. 1, Idaho National Laboratory, Idaho Cleanup Project.

NRC, 1991, *Technical Position on Waste Form*, Rev. 1, Low-Level Waste Management Branch, Nuclear Regulatory Commission, January 1991.

Pittman, John R., 1989, *Hydrological and Meteorological Data for an Unsaturated Zone Study near the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho — 1985-86*, DOE/ID-22079, U.S. Geological Survey Open-File Report 89-74, U.S. Geological Survey, U.S. Department of Energy Idaho Operations Office, and U.S. Department of the Interior.

Riley, R. G. and C. A. Lo Presti, 2004, *Recommended Parameter Values for INEEL Subsurface Disposal Area Source Release Modeling*, PNNL-14742, Pacific Northwest National Laboratory.

Salomon, Hopi, Daryl R. Haefner, Beth A. McIlwain, Jila Banaee, Jeffrey J. Einerson, and Anna K. Podgorney, 2003, *Field Sampling Plan for the OU 7-10 Glovebox Excavator Method Project*, INEEL/EXT-02-00542, Rev. 2, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Sentieri, Paul, 2003, *Criticality Safety Evaluation for In Situ Grouting in the Subsurface Disposal Area*, INEEL/EXT-03-00638, Rev. 0, Idaho National Engineering and Environmental Laboratory.

Serne, R. J., W. J. Martin, and V. L. LeGore, 1995, *Hanford Grout Technology Program: Leach Test of Cladding Removal Waste Grout Using Hanford Groundwater*, PNL-10745, Pacific Northwest Laboratory.

Serne, R. J., W. J. Martin, V. L. LeGore, C. W. Lindenmeier, S. B. McLaurine, P. F. C. Martin, and R. O. Lokken, 1989, *Leach Tests on Grouts Made with Actual and Trace Metal-Spiked Synthetic Phosphate/Sulfate Waste,* PNL-7121, Pacific Northwest Laboratory.

Shaw, P. G., 2004, "Grout Selection Criteria and Recommendation for the OU 7-13/14 In Situ Grouting Project," EDF-5333, Rev. 0, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Shaw, P. G. and J. R. Weidner, 1996, *Laboratory-Performance Criteria for In Situ Waste-Stabilization Materials*, INEL-96/0069, Idaho National Engineering Laboratory.

Stephens, D. L., 2004, "OU 7-13/14 In Situ Grouting Project Foundation Grouting Study," EDF-5028, Rev. 0, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

TerraTherm, 2005a, *Moderate Temperature ISTD Application: Chlorinated Solvents Fact Sheet*, http://www.terratherm.com/InfoSheets/TESVE%20Info%20Sheet.pdf, Web page updated 2005, Web page visited June 7, 2005.

TerraTherm, 2005b, *Bay Area Defense Conversion Action Team, Demonstration ISTD Project Fact Sheet*, http://www.terratherm.com/CaseStudies/WS%20BADCAT.pdf, Web page updated 2005, Web page visited June 7, 2005.

TerraTherm, 2005c, *Missouri Electric Works Superfund Site, Demonstration ISTD Project Fact Sheet*, http://www.terratherm.com/CaseStudies/WS%20MEW.pdf, Web page updated 2005, Web page visited June 7, 2005.

U. S. Navy, 1998, *Overview of Thermal Desorption Technology*, CR 98.008-ENV, Naval Facilities Engineering Service Center.

U. S. Navy, 1997, *A Demonstration of In Situ Thermal Desorption Thermal Blankets and Wells*, TDS-2004-ENV, Naval Facilities Engineering Service Center.

Vigil, M. J., 1990, *Subsurface Disposal Area (SDA) Waste Identification (1952 - 1970 Emphasis)*, EGG-WM-8727, Rev. 2, Idaho National Engineering Laboratory.

Vinegar, H. J., G. L. Stegemeier, and R. B. Sheldon, 1997, "Remediation of Deep Soil Using Thermal Vacuum Wells," *Society of Petroleum Engineers Annual Technical Conference*, *San Antonio, Texas*, *October 1997*, pp. 905-918.

Vinegar, H. J., E. P. Rouffignac, G. L. Stegemeier, J. M. Hirsch, and F. G. Carl, 1998, "In Situ Thermal Desorption Using Thermal Wells and Blankets," *First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18–21, 1998*, Vol. 5, Battelle Press.

Yancey, Neal A., Peter G. Shaw, David F. Nickelson, Gretchen E. Matthern, and Guy G. Loomis, 2003, *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14*, INEEL/EXT-03-00059, Rev 0, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

Zitnik, James F., Aran T. Armstrong, Brian K. Corb, Mark H. Edens, Douglas B. Holsten, Patricia M. O'Flaherty, Janet Rodriguez, Tamara N. Thomas, Russell L. Treat, Wayne Schofield, and Kira L. Sykes, 2002, *Preliminary Evaluation of Remedial Alternatives for the Subsurface Disposal Area,* INEEL/EXT-02-01258, Rev. 0, prepared by CH2MHILL for Idaho National Engineering and Environmental Laboratory.